Supporting Information

Diastereoselective Povarov-Like Reaction Involving O-Pivaloylated D-Galactosylimine

~~Diastereoselective Povarov-like Reaction Involving *O*-pivaloylated D-galactosylimine~~

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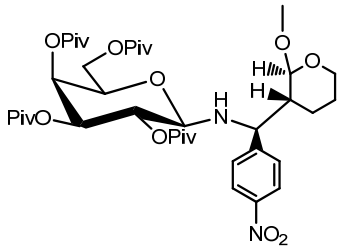
General Remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. $CHCl_3$ was distilled over P_2O_5. Reactions were monitored by thin-layer chromatography (TLC) using commercial silica gel HSGF254 plates. Column chromatography was performed on Silica Gel 60 (E. Merck, 230-400 mesh). The ^1H (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded with Bruker AM-400 spectrometer in $CDCl_3$ solution. Chemical shifts were referenced with tetramethylsilane (0 ppm for ^1H and 77.0 ppm for ^{13}C). The HR-ESI-MS data were measured on a Bruker Apex IV FTMS. Enantiomeric ratio (er) was determined with Daicel Chiralcel AS-H column (25 cm - 0.46 cm ID, n-hexane/i-PrOH = 30:70, 1 mL/min, 220 nm).

General procedure for the preparation of 4

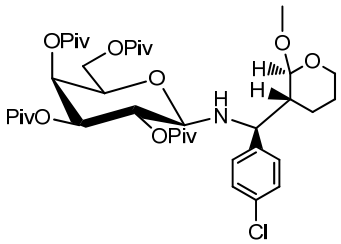
An oven-dried 10 mL vial was charged with *O*-pivaloylated β-D-galactosylimine (0.15 mmol) and $Sc(OTf)_3$ (0.075 mmol). After the vessel was treated with alternating vacuum and nitrogen purge, 1 mL of dry $CHCl_3$ was added via a syringe, and the mixture was stirred under N_2 at -40□ for 15 min before 3, 4-2*H*-pyran or 2, 3-2*H*-furan (0.15 mmol) and MeOH or *i*-PrOH (0.225 mmol, 1.5 equiv) were added. The resulting solution was stirred for the indicated time until the reaction was complete as shown by TLC (usually 24h). Then three drops of triethylamine were added and the mixture was gradually warmed to room temperature. After extracted with CH_2Cl_2, the organic layer was washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and the volatiles were removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1), yielding the corresponding compounds **4aa-gb** as a mixture of 4~8 diastereomers.

(2*S*,3*R*)-2-methoxy-3-[(*S*)-4-nitrophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-pyran (4aa)



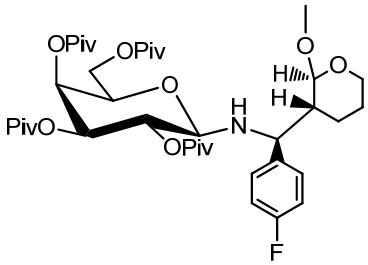
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 5.33 (d, *J* = 2.5 Hz, 1H), 5.07 (dd, *J* = 10.2, 8.8 Hz, 1H), 4.98 (dd, *J* = 10.3, 3.3 Hz, 1H), 4.34 (d, *J* = 7.6 Hz, 1H), 4.15 (dd, *J* = 11.1, 6.9 Hz, 1H), 4.03 – 3.84 (m, 3H), 3.66 (dd, *J* = 12.9, 8.5 Hz, 2H), 3.53 (s, 3H), 3.23 (d, *J* = 12.9 Hz, 1H), 1.86 – 1.62 (m, *J* = 11.6, 7.5, 3.8 Hz, 1H), 1.55 – 1.31 (m, 3H), 1.27 (s, 9H), 1.21 (s, 9H), 1.19 (s, 9H), 1.09 (s, 9H), 1.01 – 0.74 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.85, 177.28, 177.10, 176.77, 148.51, 147.45, 129.49, 123.34, 105.59, 86.22, 71.57, 71.37, 68.88, 67.32, 65.22, 61.66, 57.97, 55.71, 45.32, 39.03, 38.78, 38.70, 38.68, 27.27, 27.17, 27.11, 27.06, 24.83, 24.43. **HR-ESI-MS**: Calcd for $C_{39}H_{60}N_2O_{13}$ $[M+H]^+$: 765.4168, found: 765.4156.

(2*S*,3*R*)-2-methoxy-3-[(*S*)-4-chlorophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-pyran (4ba)



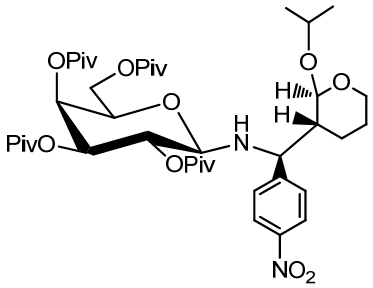
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.32 (d, *J* = 2.5 Hz, 1H), 5.06 (dd, *J* = 10.3, 7.6 Hz, 1H), 4.98 (dd, *J* = 10.3, 3.3 Hz, 1H), 4.22 (d, *J* = 7.5 Hz, 1H), 4.13 (dd, *J* = 11.1, 6.9 Hz, 1H), 3.99 – 3.88 (m, 3H), 3.74 – 3.61 (m, 2H), 3.51 (s, 3H), 3.04 (d, *J* = 12.8 Hz, 1H), 1.70 – 1.60 (m, *J* = 15.5, 7.6, 3.9 Hz, 1H), 1.50 – 1.37 (m, 3H), 1.26 (s, 9H), 1.20 (s, 9H), 1.18 (s, 9H), 1.09 (s, 9H), 0.82 – 0.74 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.89, 177.32, 177.12, 176.83, 138.84, 133.07, 130.10, 128.26, 105.75, 86.13, 71.48, 71.45, 68.92, 67.47, 65.23, 61.78, 57.61, 55.69, 45.40, 39.04, 38.76, 38.71, 38.69, 27.27, 27.19, 27.13, 27.08, 24.92, 24.23. **HR-ESI-MS**: Calcd for $C_{39}H_{60}ClNO_{11}$ $[M+H]^+$: 754.3927, found: 754.3913.

(2*S*,3*R*)-2-methoxy-3-[(*S*)-4-fluorophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-pyran (4ca)



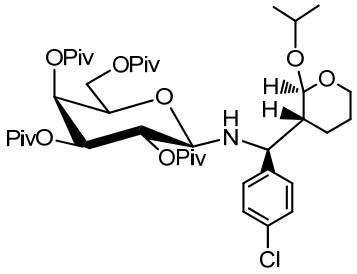
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.6, 5.6 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 5.32 (d, *J* = 2.5 Hz, 1H), 5.06 (dd, *J* = 11.7, 7.3 Hz, 1H), 4.98 (dd, *J* = 10.3, 3.3 Hz, 1H), 4.21 (d, *J* = 7.5 Hz, 1H), 4.13 (dd, *J* = 11.1, 6.9 Hz, 1H), 4.01 – 3.89 (m, 3H), 3.75 – 3.61 (m, 2H), 3.51 (s, 3H), 3.06 (d, *J* = 12.8 Hz, 1H), 1.69 – 1.61 (m, 1H), 1.49 – 1.36 (m, 3H), 1.27 (s, 9H), 1.21 (s, 9H), 1.18 (s, 9H), 1.09 (s, 9H), 0.95 – 0.85 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.90, 177.31, 177.15, 176.84, 135.93, 135.90, 130.19, 130.12, 115.01, 114.80, 105.83, 86.13, 71.50, 71.41, 68.90, 67.47, 65.19, 61.78, 57.57, 55.68, 45.45, 39.03, 38.75, 38.70, 27.25, 27.18, 27.12, 27.07, 24.90, 24.26. **HR-ESI-MS**: Calcd for $C_{39}H_{60}FNO_{11}$ $[M+H]^+$: 738.4223, found: 738.4213.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-nitrophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-pyran (4da)



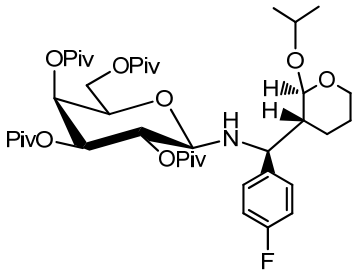
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 5.35 (d, *J* = 2.7 Hz, 1H), 5.10 (dd, 1H), 4.95 (dd, *J* = 10.3, 3.4 Hz, 1H), 4.34 (d, *J* = 7.9 Hz, 1H), 4.23 – 4.02 (m, 4H), 3.92 (dd, *J* = 11.1, 7.2 Hz, 2H), 3.63 (t, *J* = 7.0 Hz, 1H), 3.58 – 3.49 (m, 1H), 3.35 (td, *J* = 11.5, 3.1 Hz, 1H), 1.76 – 1.59 (m, 1H), 1.47 – 1.39 (m, 1H), 1.37 (d, *J* = 1.4 Hz, 3H), 1.36 (d, *J* = 1.5 Hz, 3H), 1.25 (s, 9H), 1.20 (s, 9H), 1.20 (s, 9H), 1.08 (s, 9H), 1.01 – 0.72 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.90, 177.08, 177.03, 176.77, 149.06, 147.50, 129.53, 123.48, 103.98, 86.29, 71.53, 71.33, 70.62, 68.52, 67.37, 65.54, 61.55, 59.38, 45.11, 38.99, 38.76, 38.73, 38.68, 27.29, 27.15, 27.08, 26.63, 25.00, 23.78, 21.73. **HR-ESI-MS**: Calcd for $C_{41}H_{64}N_2O_{13}$ $[M+H]^+$: 793.4481, found: 793.4460.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-chlorophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-pyran (4ea)



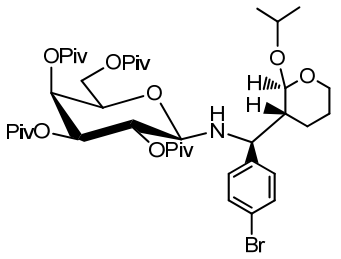
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 5.34 (d, *J* = 2.7 Hz, 1H), 5.09 (dd, *J* = 10.1, 9.2 Hz, 1H), 4.96 (dd, *J* = 10.3, 3.4 Hz, 1H), 4.31 (d, *J* = 7.9 Hz, 1H), 4.16 – 3.94 (m, 4H), 3.94 – 3.88 (m, 2H), 3.73 – 3.52 (m, 2H), 3.33 (td, *J* = 11.4, 2.9 Hz, 1H), 1.69 – 1.60 (m, 1H), 1.36 (d, *J* = 1.6 Hz, 3H), 1.35 (d, *J* = 1.6 Hz, 3H), 1.25 (s, 9H), 1.20 (s, 9H), 1.19 (s, 9H), 1.08 (s, 9H), 0.99 – 0.86 (m, 2H), 0.86 – 0.76 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.91, 177.09, 177.06, 176.80, 139.49, 133.04, 130.08, 128.33, 104.29, 86.20, 71.43, 71.34, 70.58, 68.55, 67.50, 65.59, 61.65, 59.13, 45.17, 39.02, 38.98, 38.71, 38.66, 27.27, 27.14, 27.13, 27.07, 26.60, 25.12, 23.78, 21.73. **HR-ESI-MS**: Calcd for $C_{41}H_{64}ClNO_{11}$ $[M+H]^+$: 782.4240, found: 782.4225.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-fluorophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-pyran (4fa)



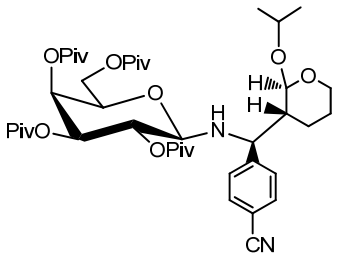
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.5, 5.6 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 5.34 (d, *J* = 2.9 Hz, 2H), 5.09 (dd, *J* = 11.6, 7.7 Hz, 2H), 4.96 (dd, *J* = 10.3, 3.4 Hz, 1H), 4.32 (d, *J* = 7.8 Hz, 1H), 4.18 – 3.98 (m, 3H), 3.97 – 3.86 (m, 3H), 3.73 – 3.52 (m, 2H), 3.33 (td, *J* = 11.4, 2.9 Hz, 1H), 1.74 – 1.51 (m, 2H), 1.36 (d, *J* = 2.0 Hz, 3H), 1.35 (d, *J* = 2.1 Hz, 3H), 1.25 (s, 9H), 1.20 (s, 9H), 1.18 (s, 9H), 1.08 (s, 9H), 1.00 – 0.72 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.94, 177.14, 177.07, 176.82, 136.56, 130.18, 130.10, 115.09, 114.88, 104.35, 86.21, 71.49, 71.33, 70.58, 68.56, 67.53, 65.58, 61.68, 59.04, 45.27, 38.99, 38.71, 38.67, 27.26, 27.15, 27.13, 27.08, 26.61, 25.15, 23.79, 21.73. **HR-ESI-MS**: Calcd for $C_{41}H_{64}FNO_{11}$ $[M+H]^+$: 766.4536, found: 766.4517.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-bromophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-pyran (4ga)



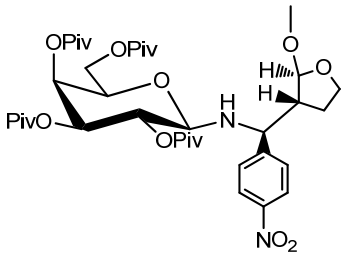
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 5.34 (d, *J* = 2.7 Hz, 1H), 5.09 (dd, *J* = 11.3, 8.0 Hz, 1H), 4.96 (dd, *J* = 10.3, 3.4 Hz, 1H), 4.31 (d, *J* = 7.9 Hz, 1H), 4.19 – 4.05 (m, 2H), 4.04 – 3.96 (m, 1H), 3.95 – 3.84 (m, 3H), 3.73 – 3.51 (m, 2H), 3.33 (td, *J* = 11.4, 3.0 Hz, 1H), 1.66 – 1.55 (m, 1H), 1.47 – 1.37 (m, 2H), 1.36 (d, *J* = 1.1 Hz, 3H), 1.34 (d, *J* = 1.3 Hz, 3H), 1.25 (s, 9H), 1.20 (s, 9H), 1.19 (s, 9H), 1.08 (s, 9H), 0.94 – 0.75 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.90, 177.07, 177.05, 176.79, 140.03, 131.28, 130.47, 121.14, 104.27, 86.19, 71.42, 71.34, 70.57, 68.54, 67.50, 65.58, 61.65, 59.18, 45.12, 38.97, 38.70, 38.65, 27.26, 27.13, 27.12, 27.07, 26.58, 25.11, 23.77, 21.72. **HR-ESI-MS**: Calcd for $C_{41}H_{64}BrNO_{11}$ $[M+H]^+$: 826.3735, found: 826.3721.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-cyanophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-pyran (4ha)



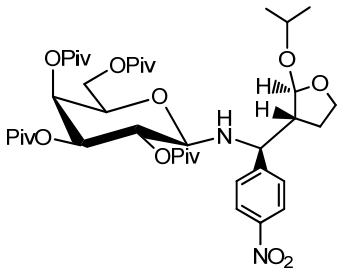
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.35 (d, *J* = 2.6 Hz, 1H), 5.09 (dd, *J* = 10.2, 9.0 Hz, 1H), 4.96 (dd, *J* = 10.3, 3.4 Hz, 1H), 4.33 (d, *J* = 7.9 Hz, 1H), 4.18 – 4.05 (m, 3H), 4.02 (d, *J* = 9.0 Hz, 1H), 3.97 – 3.86 (m, 2H), 3.78 – 3.67 (m, 2H), 3.63 (t, *J* = 7.2 Hz, 1H), 3.53 (dd, *J* = 13.1, 8.9 Hz, 1H), 3.35 (td, *J* = 11.4, 3.1 Hz, 1H), 1.37 (d, 3H), 1.35 (d, *J* = 0.9 Hz, 3H), 1.25 (s, 9H), 1.20 (s, 9H), 1.19 (s, 9H), 1.08 (s, 9H), 1.05 – 0.97 (m, 1H), 0.93 – 0.77 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.91, 177.10, 177.01, 176.77, 146.96, 132.04, 129.50, 118.70, 111.46, 104.03, 86.27, 71.45, 71.33, 70.61, 68.50, 67.35, 65.55, 61.53, 59.65, 58.45, 45.03, 38.98, 38.73, 38.72, 38.67, 27.27, 27.13, 27.13, 27.07, 26.63, 25.01, 23.77, 21.72, 18.42. **HR-ESI-MS**: Calcd for $C_{42}H_{64}N_2O_{11}$ $[M+H]^+$: 773.4582, found: 773.4574.

(2*S*,3*R*)-2-methoxy-3-[(*S*)-4-nitrophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-furan (4ab)



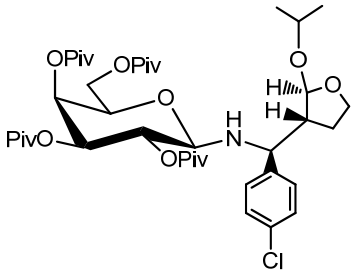
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 5.36 (d, *J* = 2.2 Hz, 1H), 5.07 (dd, *J* = 10.3, 8.2 Hz, 1H), 5.02 (dd, *J* = 3.1, 10.3 Hz,, 1H), 4.94 (d, *J* = 3.5 Hz, 1H), 4.17 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.09 (d, *J* = 9.7 Hz, 1H), 3.96 (dd, *J* = 11.1, 6.9 Hz, 1H), 3.90 – 3.67 (m, 4H), 3.43 (s, 3H), 2.37 – 2.15 (m, *J* = 17.4, 9.4, 3.5 Hz, 1H), 1.63 – 1.48 (m, 1H), 1.48 – 1.33 (m, *J* = 9.5, 7.1, 6.5 Hz, 1H), 1.28 (s, 9H), 1.21 (s, 9H), 1.15 (s, 9H), 1.10 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.81, 177.38, 177.09, 176.73, 149.62, 147.52, 128.71, 123.64, 108.40, 86.47, 71.60, 71.30, 68.78, 67.15, 66.69, 61.43, 59.36, 55.47, 52.08, 39.03, 38.75, 38.69, 29.44, 27.29, 27.20, 27.17, 27.09, 27.04. **HR-ESI-MS**: Calcd for $C_{38}H_{57}N_2O_{13}$ $[M+H]^+$: 751.4011, found: 751.3995.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-nitrophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactosylamino)methyl]tetrahydro-*2H*-furan (4db)



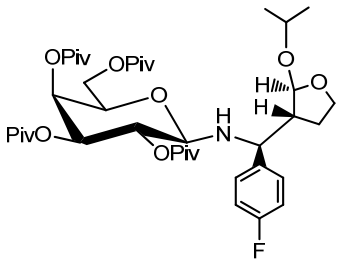
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 2H), 5.37 (d, *J* = 2.2 Hz, 1H), 5.15 (d, *J* = 4.4 Hz, 1H), 5.11 – 4.96 (m, 2H), 4.19 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.11 (d, *J* = 10.4 Hz, 1H), 4.04 – 3.90 (m, 2H), 3.89 – 3.67 (m, 4H), 2.38 – 2.07 (m, 1H), 1.49 – 1.35 (m, 2H), 1.33 (d, *J* = 6.1 Hz, 3H), 1.28 (d, *J* = 6.1 Hz, 3H), 1.26 (s, 9H), 1.21 (s, 9H), 1.17 (s, 9H), 1.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.84, 177.27, 177.08, 176.74, 149.77, 147.58, 128.73, 123.64, 105.91, 86.44, 71.71, 71.27, 70.44, 68.54, 67.23, 66.56, 61.46, 59.68, 51.85, 39.00, 38.77, 38.74, 38.70, 30.02, 27.26, 27.14, 27.12, 27.07, 23.58, 21.96. **HR-ESI-MS**: Calcd for $C_{40}H_{62}FNO_{11}$ $[M+H]^+$: 779.4324, found: 779.4306.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-chlorophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactos ylamino)methyl]tetrahydro-*2H*-furan (4eb)



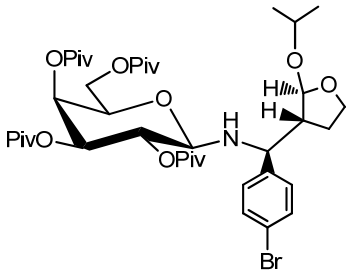
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 5.36 (d, *J* = 2.6 Hz, 1H), 5.11 (d, *J* = 4.4 Hz, 1H), 5.09 – 4.98 (m, 2H), 4.16 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.03 – 3.89 (m, 3H), 3.87 – 3.66 (m, 4H), 2.31 – 2.10 (m, 1H), 1.52 – 1.40 (m, *J* = 16.1, 5.7 Hz, 2H), 1.33 (d, *J* = 2.9 Hz, 3H), 1.27 (d, *J* = 2.9 Hz, 3H), 1.25 (s, 9H), 1.21 (s, 9H), 1.16 (s, 9H), 1.09 (s, 9H), 0.94 – 0.72 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.87, 177.32, 177.09, 176.78, 140.39, 133.27, 129.32, 128.48, 106.11, 86.26, 71.56, 71.35, 70.36, 68.55, 67.37, 66.56, 61.58, 59.48, 51.95, 39.00, 38.74, 38.72, 38.69, 30.04, 29.68, 27.24, 27.14, 27.13, 27.08, 23.60, 21.93. **HR-ESI-MS**: Calcd for $C_{40}H_{62}ClNO_{11}$ $[M+H]^+$: 768.4084, found: 768.4067.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-fluorophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galactos ylamino)methyl]tetrahydro-*2H*-furan (4fb)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 8.5, 5.5 Hz, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 5.36 (d, *J* = 2.2 Hz, 1H), 5.11 (d, *J* = 4.4 Hz, 1H), 5.08 – 4.97 (m, 2H), 4.17 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.04 – 3.89 (m, 3H), 3.85 – 3.67 (m, *J* = 19.5, 9.2, 5.0 Hz, 4H), 2.30 – 2.11 (m, 1H), 1.50 – 1.35 (m, 2H), 1.33 (d, *J* = 6.1 Hz, 3H), 1.27 (d, *J* = 6.1 Hz, 3H), 1.25 (s, 9H), 1.21 (s, 9H), 1.15 (s, 9H), 1.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.89, 177.33, 177.12, 176.81, 137.54, 137.51, 129.48, 129.40, 115.24, 115.03, 106.15, 86.24, 71.52, 71.36, 70.36, 68.54, 67.37, 66.58, 61.59, 59.41, 52.06, 39.00, 38.73, 38.69, 30.09, 27.23, 27.14, 27.12, 27.07, 23.61, 21.94. **HR-ESI-MS**: Calcd for $C_{40}H_{62}FNO_{11}$ $[M+H]^+$: 752.4379, found: 752.4363.

(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-bromophenyl(2,3,4,6-tetra-*O*-pivaloyl-β-D-galacto sylamino)methyl]tetrahydro-*2H*-furan (4gb)

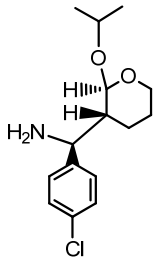


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.36 (d, *J* = 2.1 Hz, 1H), 5.11 (d, *J* = 4.4 Hz, 1H), 5.08 – 4.98 (m, 2H), 4.16 (dd, *J* = 11.1, 6.8 Hz, 1H), 4.03 – 3.89 (m, 3H), 3.85 – 3.69 (m, 4H), 2.32 – 2.08 (m, 1H), 1.50 – 1.35 (m, 2H), 1.33 (d, *J* = 6.1 Hz, 3H), 1.27 (d, *J* = 6.1 Hz, 3H), 1.25 (s, 9H), 1.21 (s, 9H), 1.16 (s, 9H), 1.09 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.88, 177.34, 177.09, 176.79, 140.91, 131.44, 129.70, 121.37, 106.09, 86.25, 71.56, 71.34, 70.37, 68.55, 67.36, 66.57, 61.58, 59.53, 51.89, 39.00, 38.74, 38.72, 38.69, 30.04, 29.68, 27.25, 27.14, 27.13, 27.08, 23.60, 21.93. **HR-ESI-MS**: Calcd for $C_{40}H_{62}BrNO_{11}$ $[M+H]^+$: 812.3579, found: 812.3570.

General procedure for the release of the chiral auxiliary

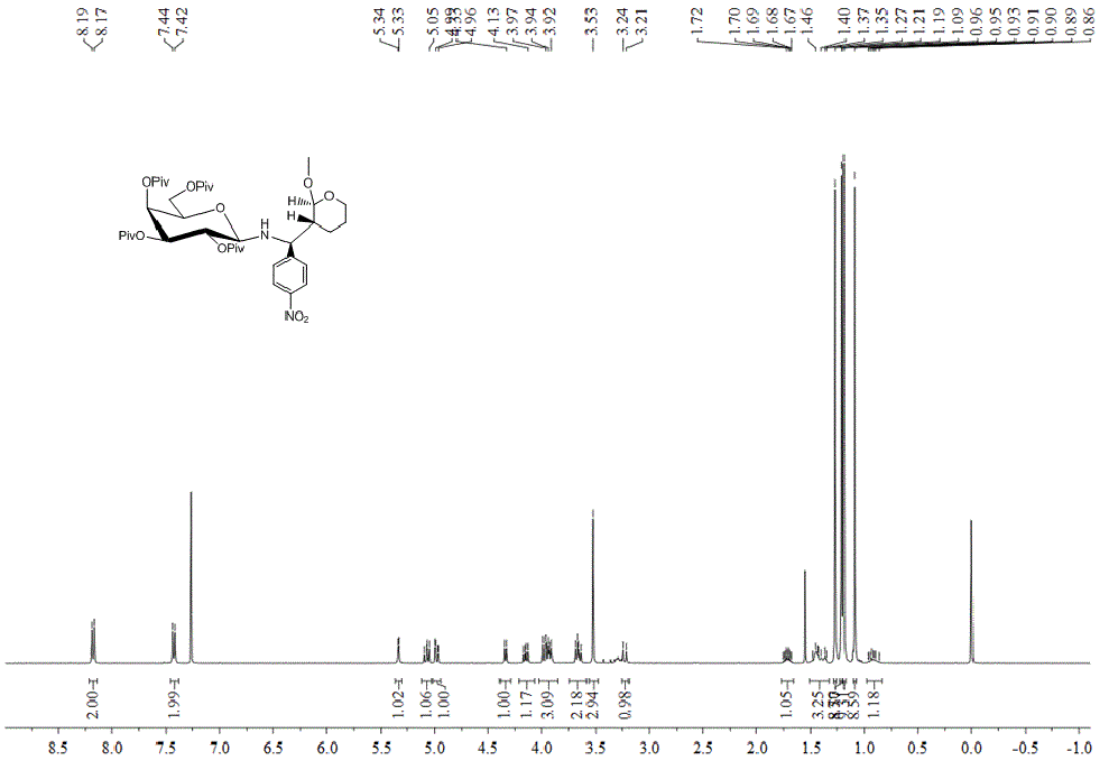
A solution of compound **4ea** (0.15mmol) in dry methanol (1.5 mL) was treated with a freshly prepared (0.5 M) solution of sodium methoxide (1 mL), which was prepared from sodium and dry methanol. The solution was stirred until the reactant was consumed (TLC control). After few drops of water added, the solution was neutralized with acetic acid. Then the solution was stirred for another 4 h. The solution was extracted with EtOAc, washed with saturated aqueous $NaHCO_3$, dried over $MgSO_4$, filtered, and the volatiles were removed under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1/2, with 0.1% Et_3N), yielding the corresponding compound **5ea**.

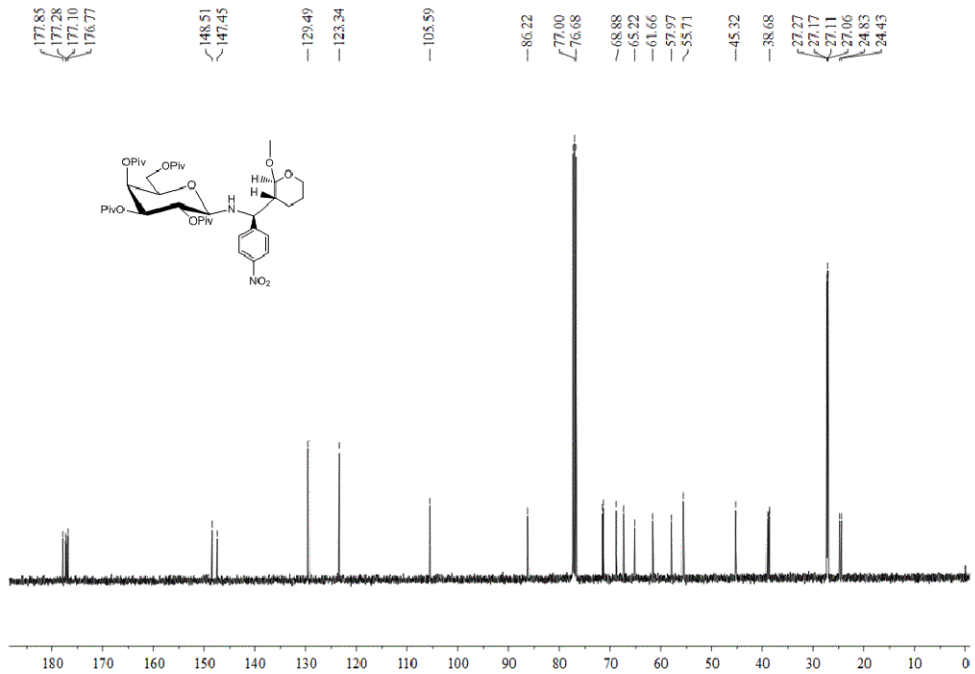
(2*R*,3*R*)-2-isopropoxy-3-[(*S*)-4-chlorophenyl(amino)methyl]tetrahydro-*2H*-pyran (5ea)

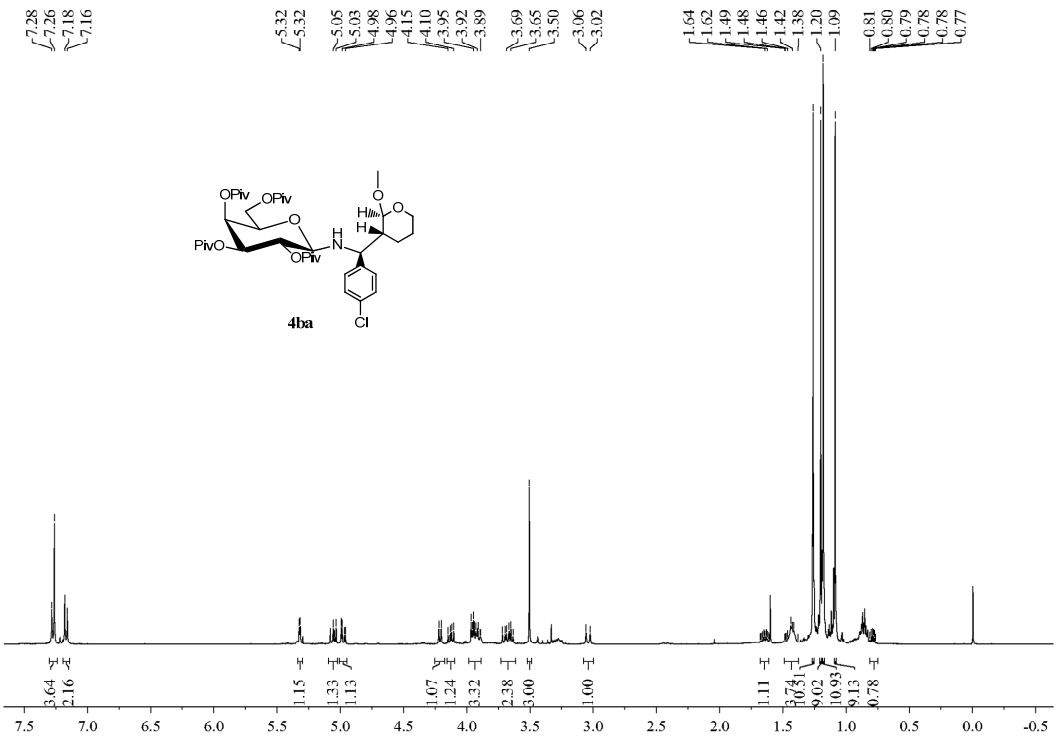


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 4.51 (d, *J* = 6.1 Hz, 1H), 4.42 – 4.20 (m, 1H), 4.13 – 3.98 (m, 1H), 3.97 – 3.87 (m, 1H), 3.58 – 3.25 (m, 1H), 1.61 – 1.36 (m, 4H), 1.25 (dd, *J* = 18.7, 6.1 Hz, 7H), 1.12 (d, *J* = 6.1 Hz, 1H), 1.01 – 0.82 (m, 1H) **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.78, 132.68, 128.82, 128.45, 101.27, 69.33, 63.90, 56.38, 46.77, 24.04, 23.92, 23.71, 21.67. **HR-ESI-MS**: Calcd for $C_{15}H_{22}ClNO_2$ $[M+H]^+$: 284.1411, found: 284.1411.

Copies of NMR spectra of 4 and 5



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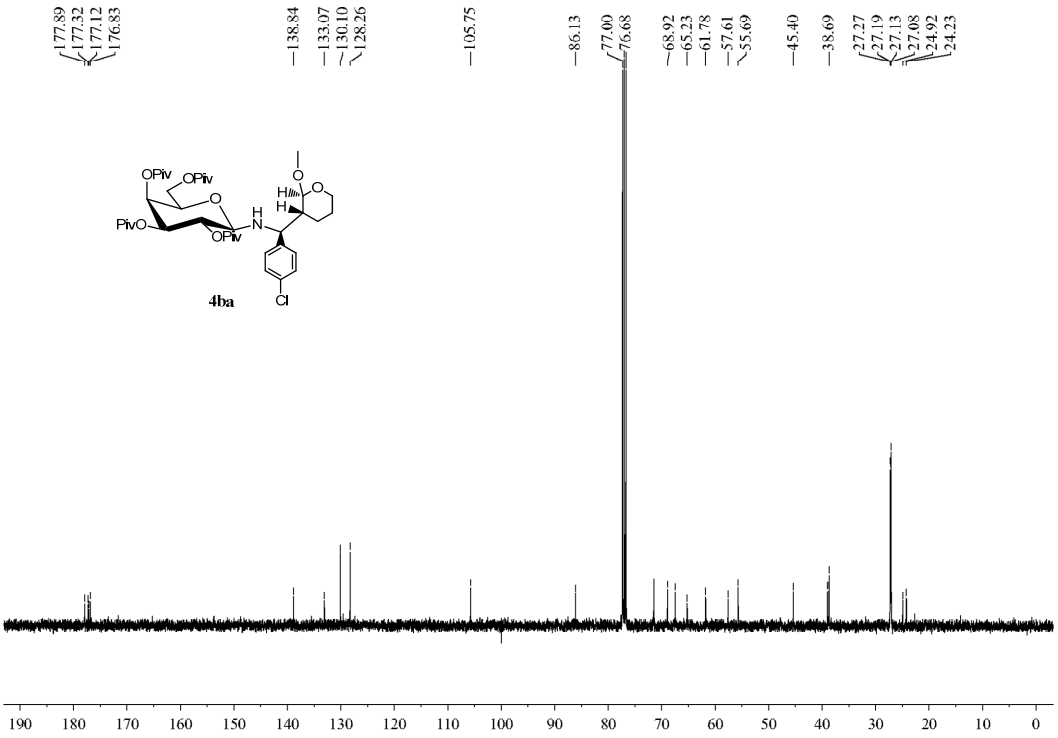
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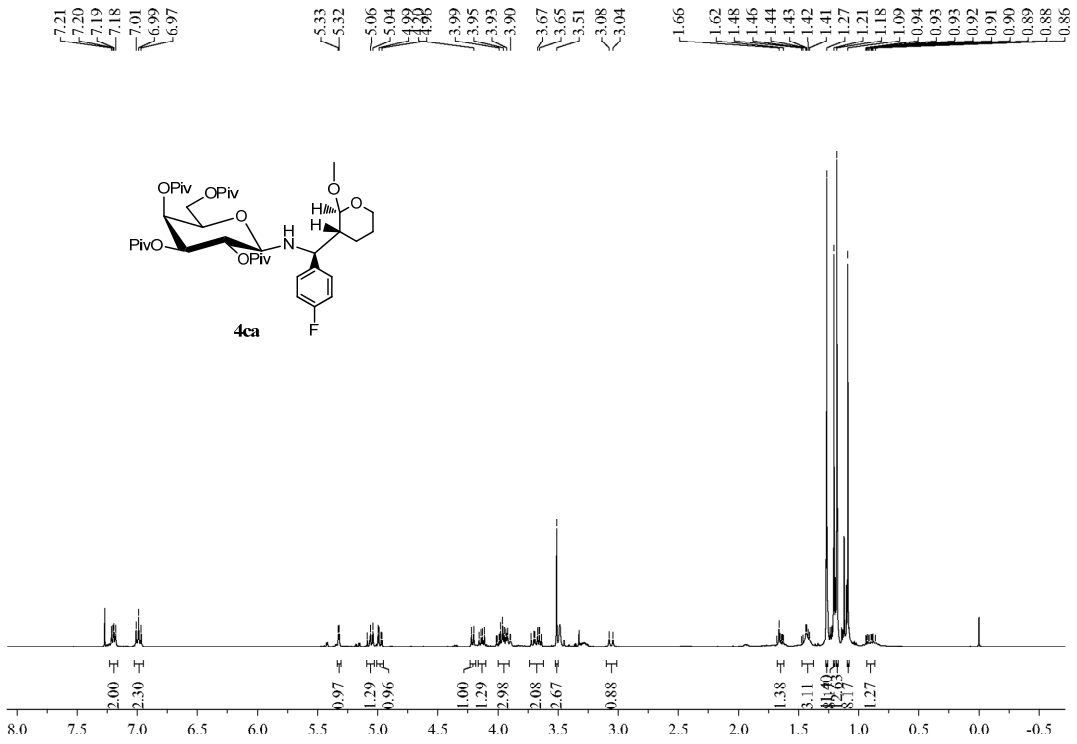
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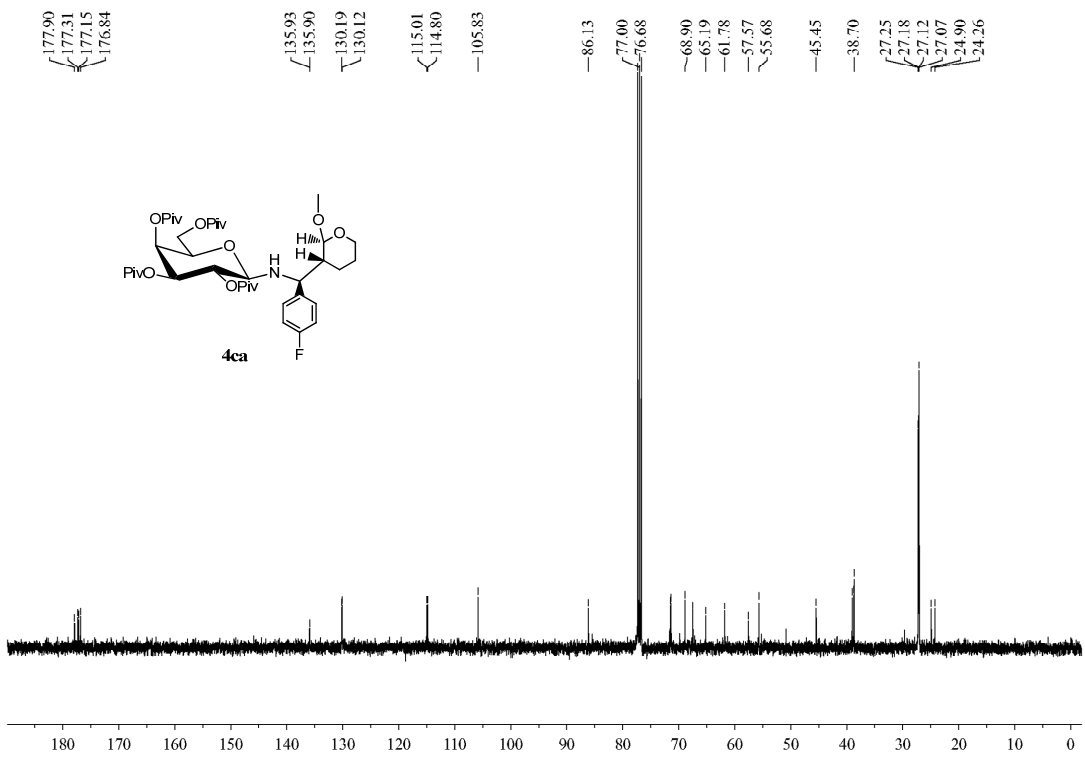
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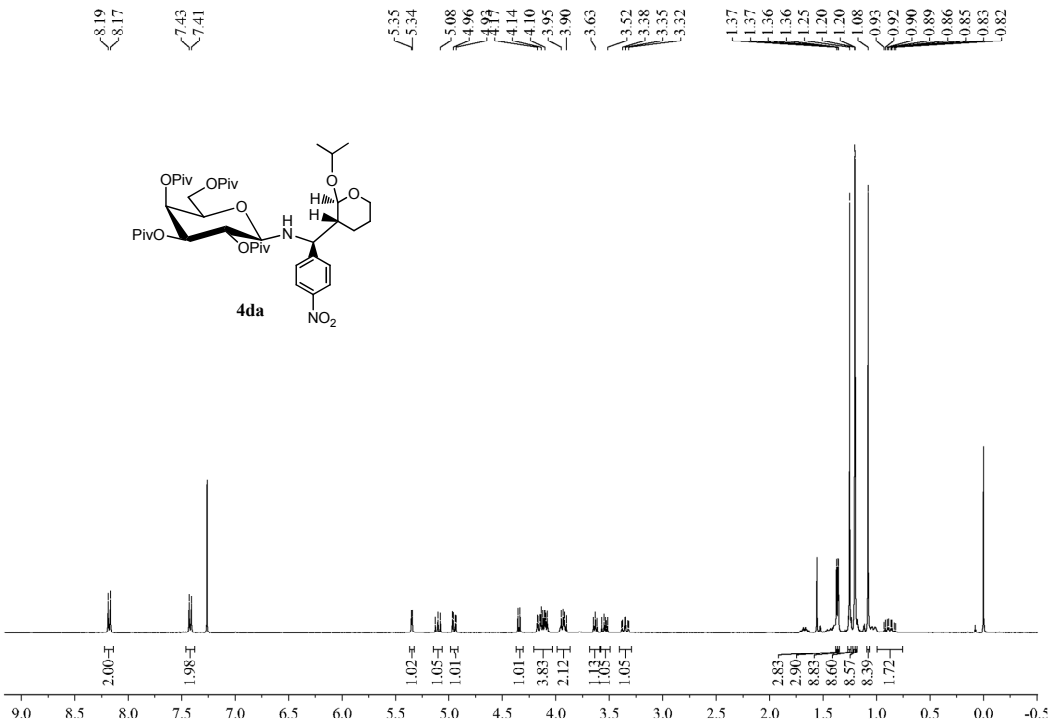
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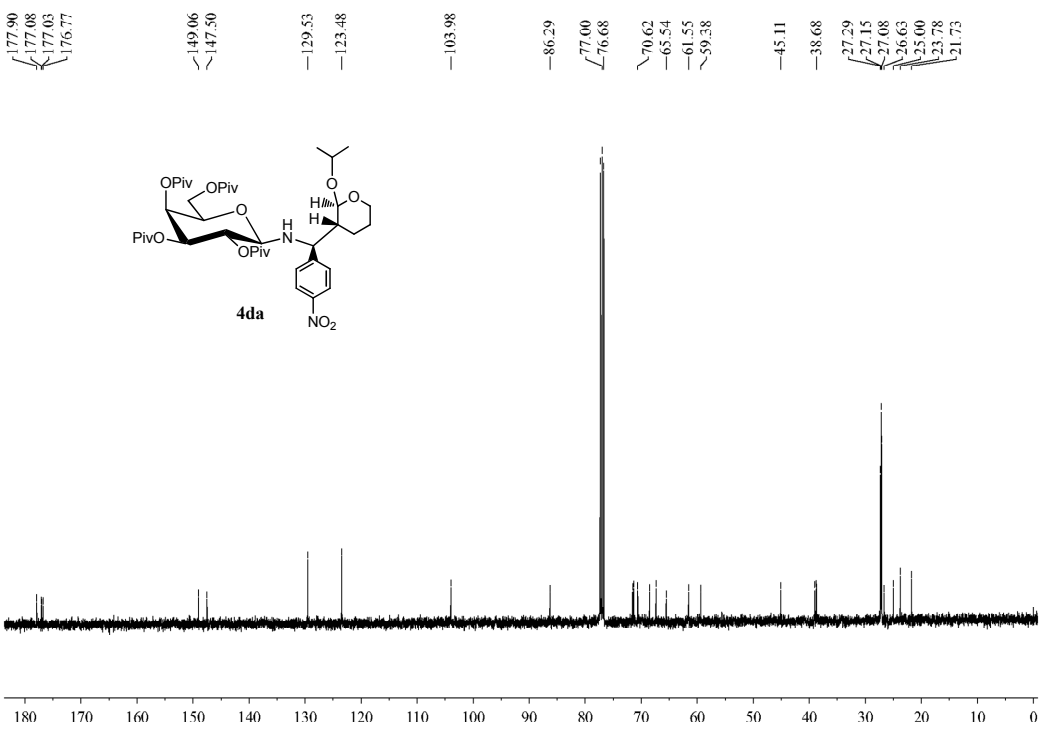
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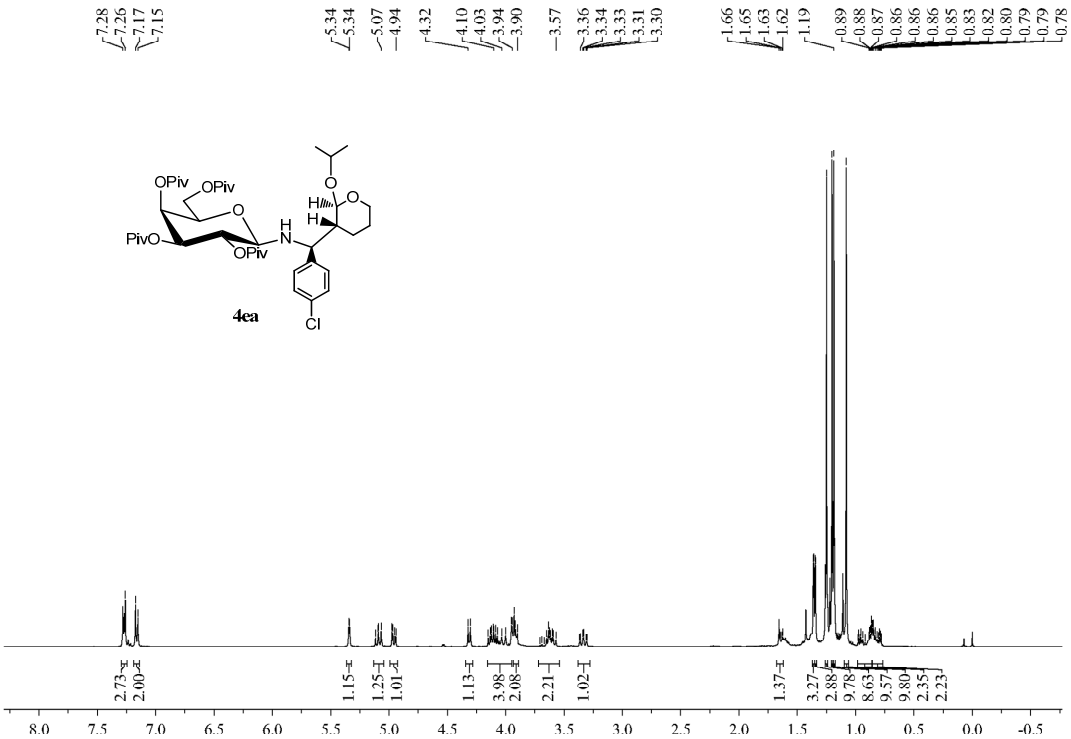
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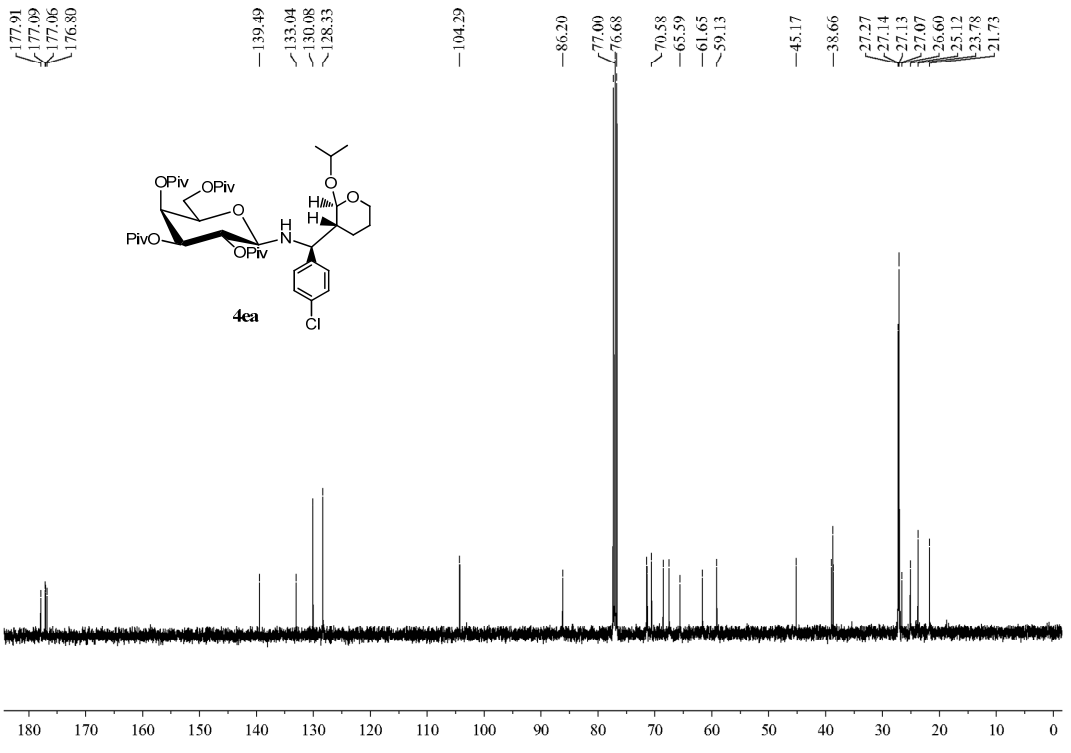
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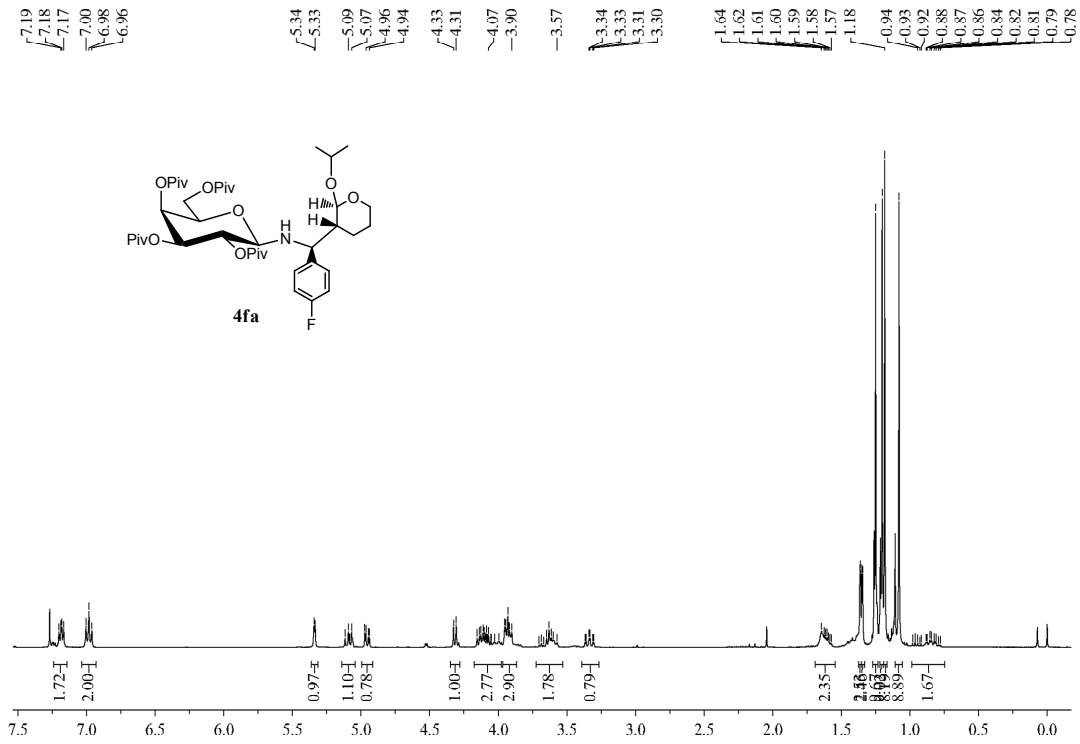
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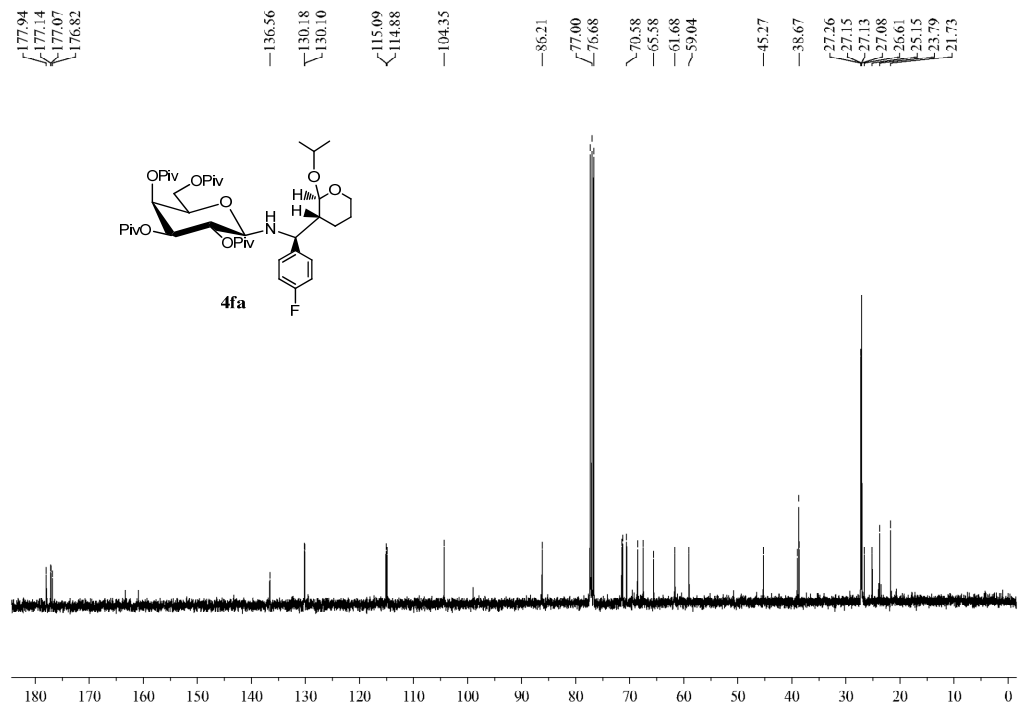
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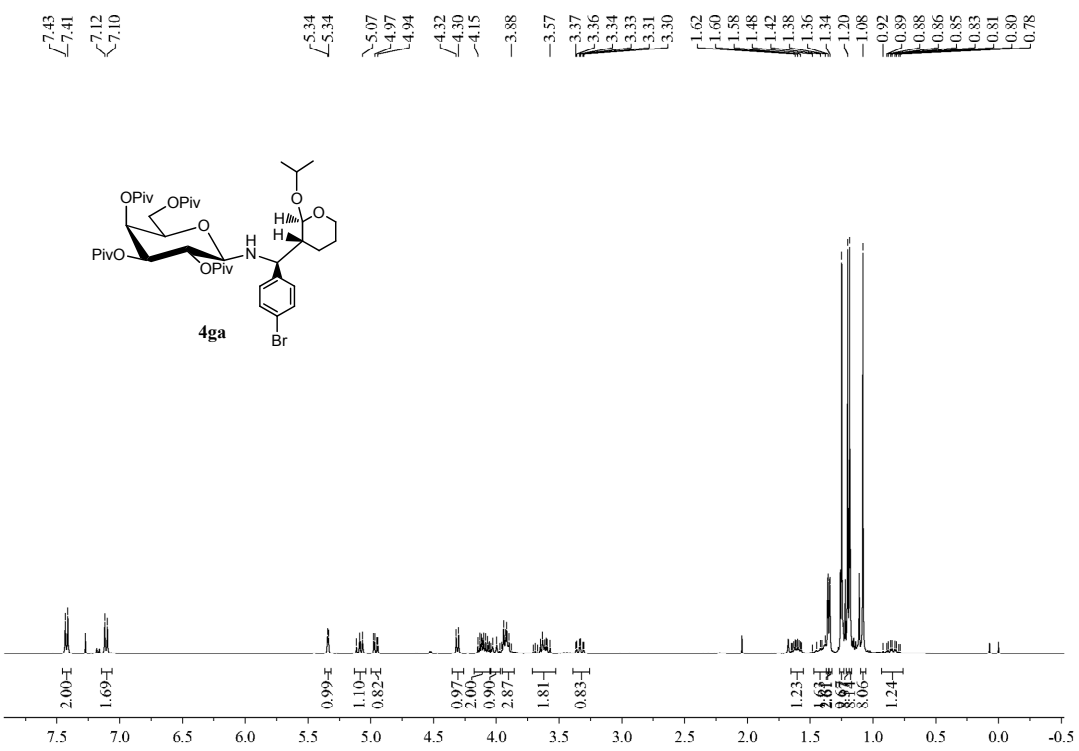
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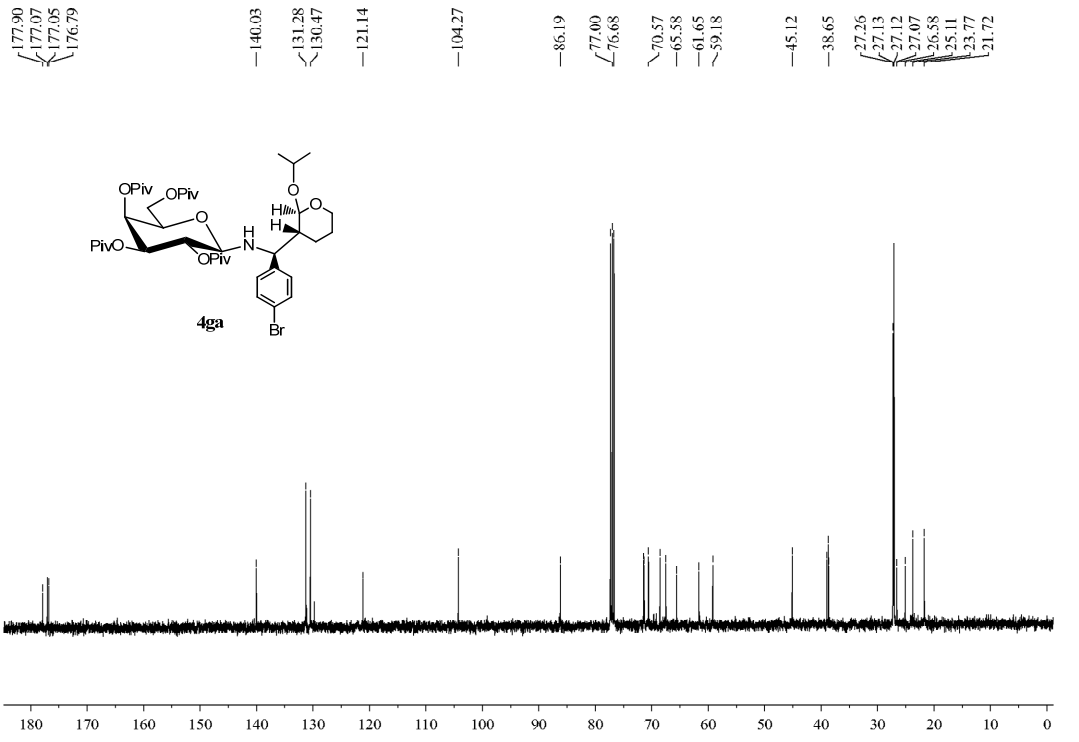
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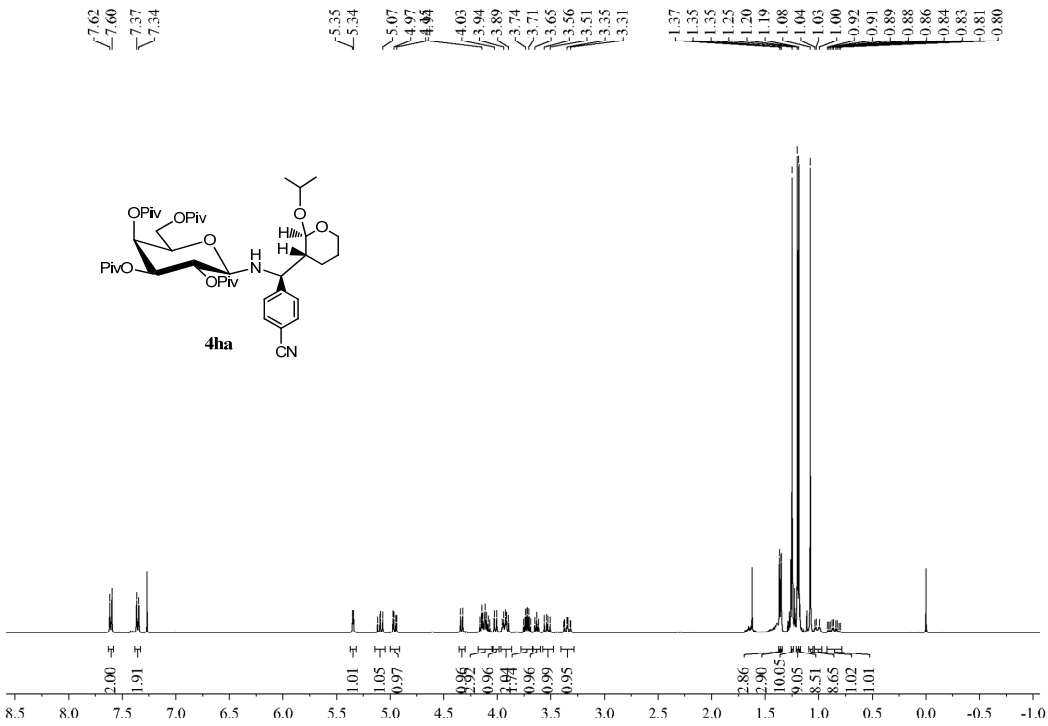
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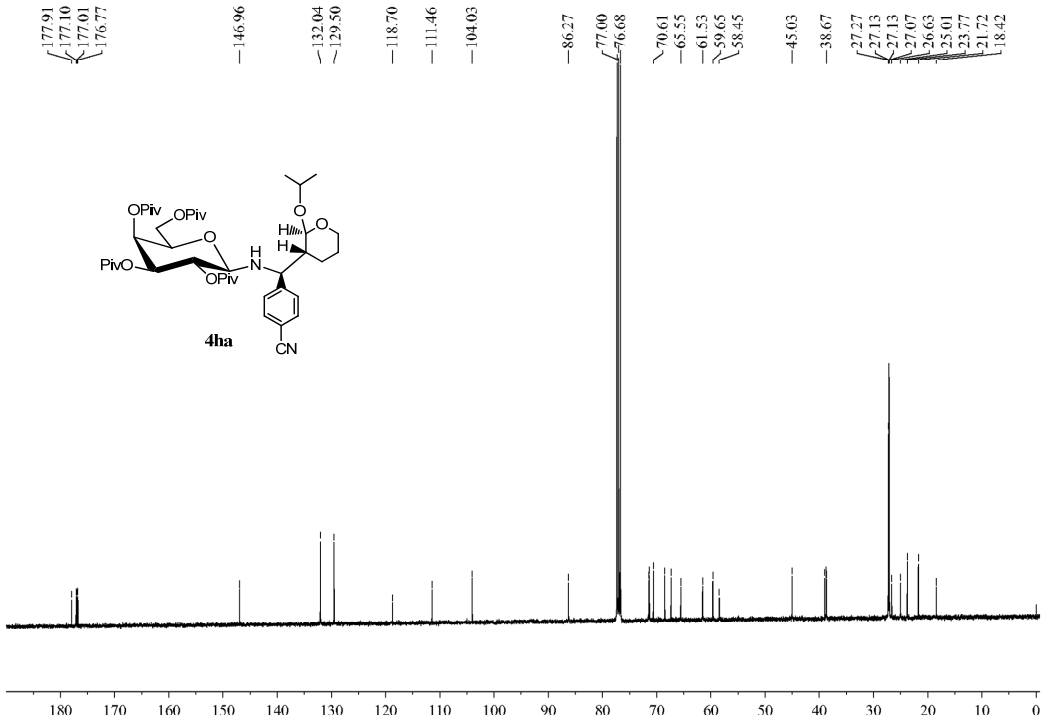
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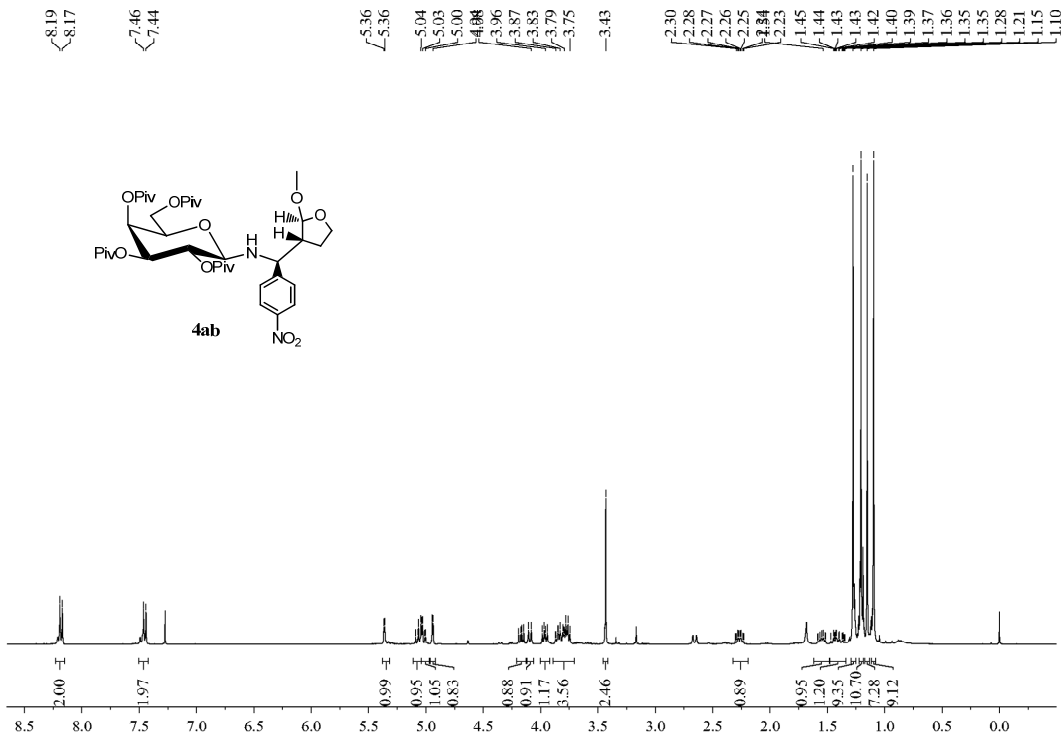
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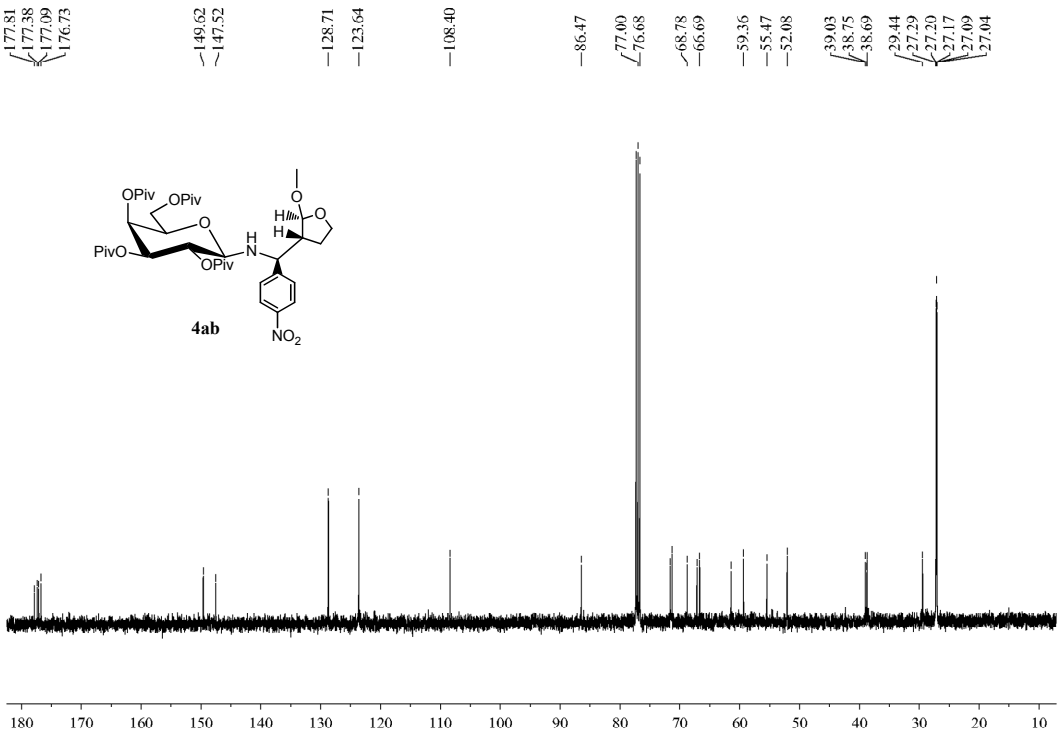
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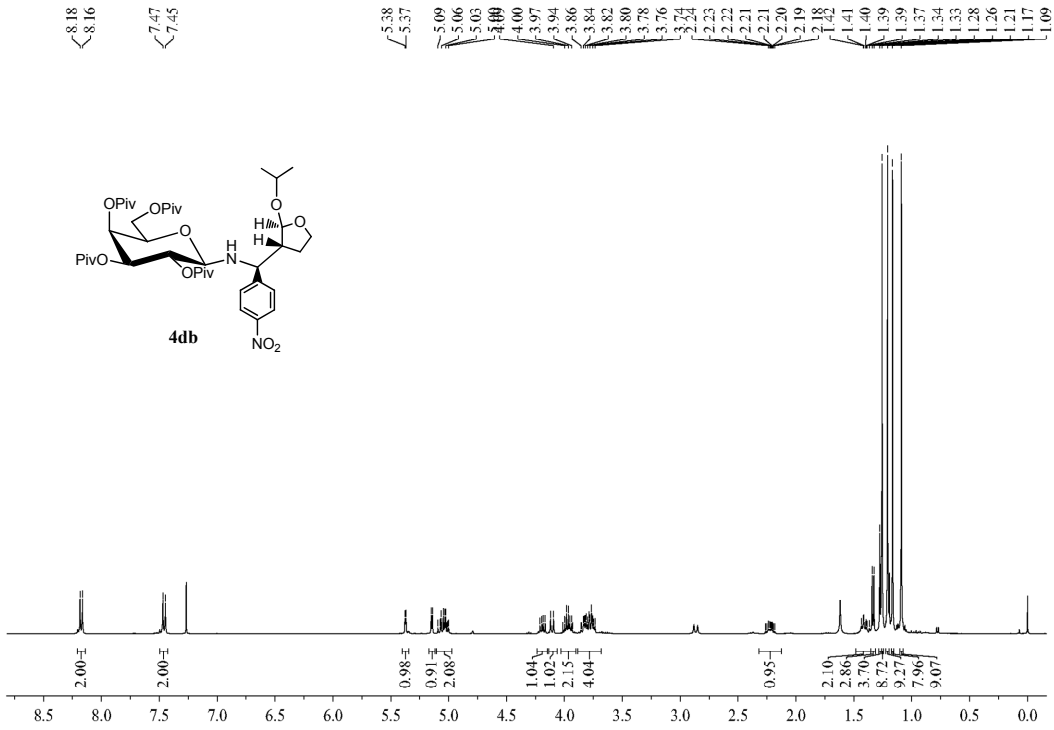
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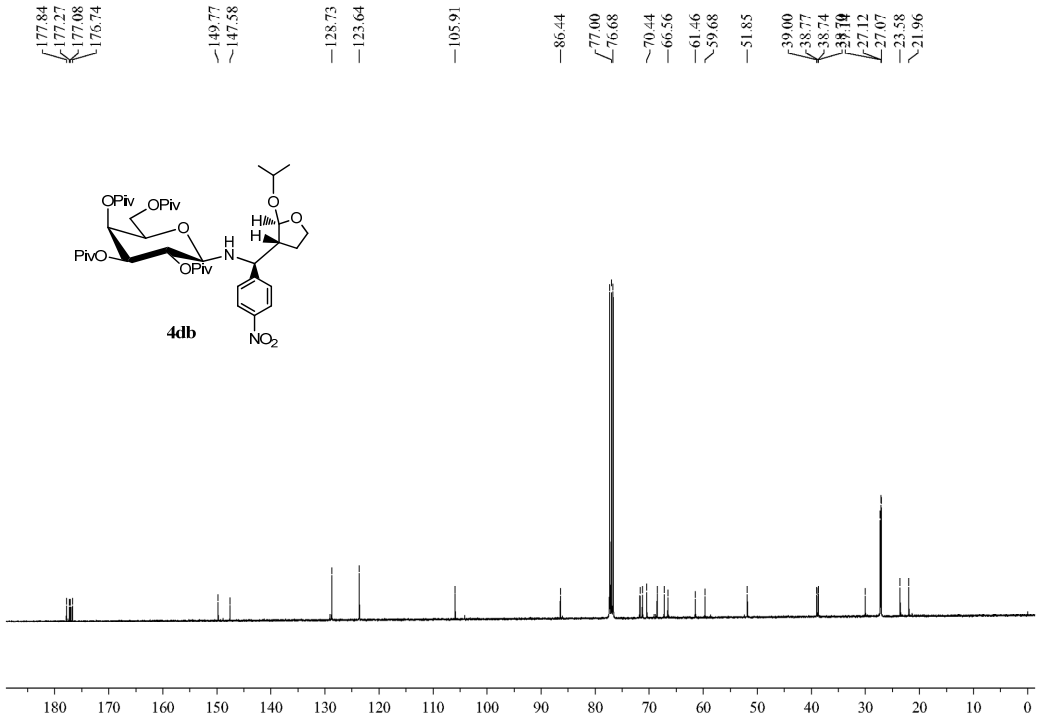
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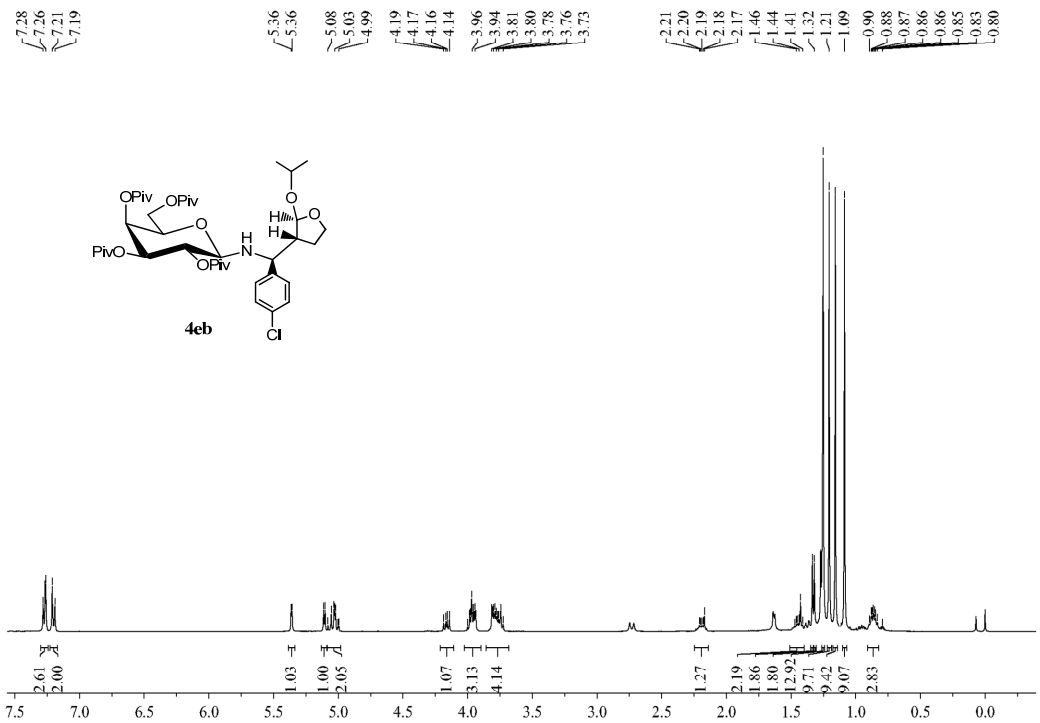
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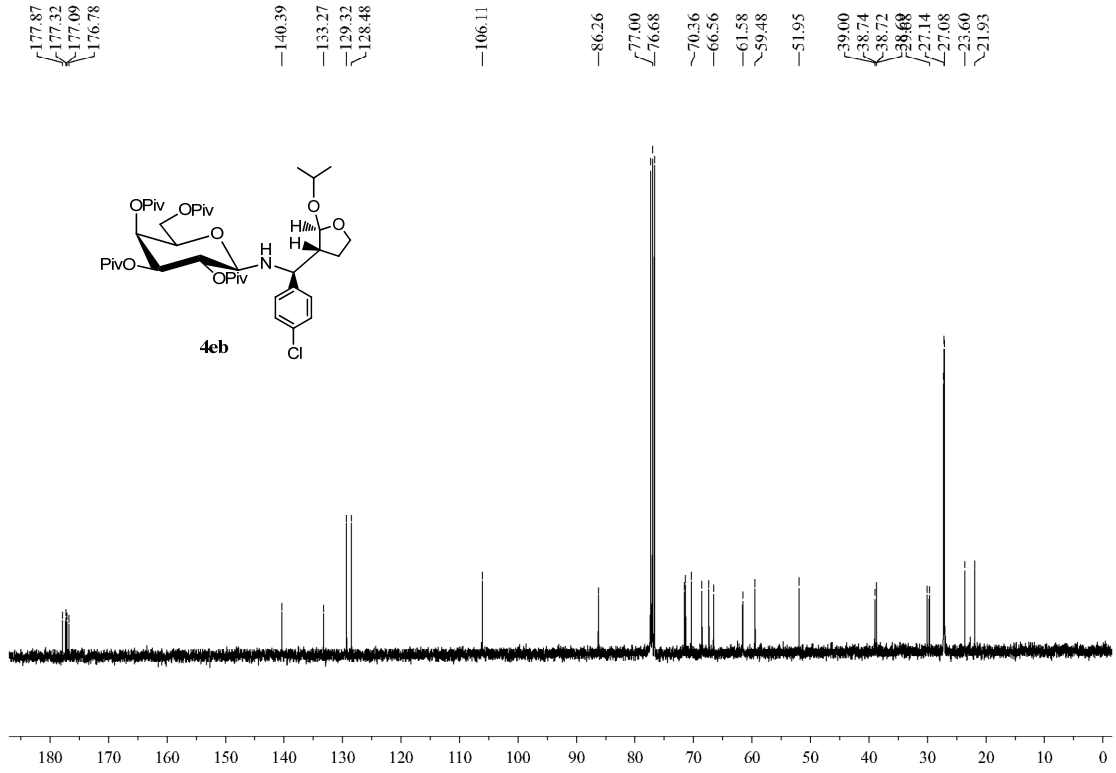
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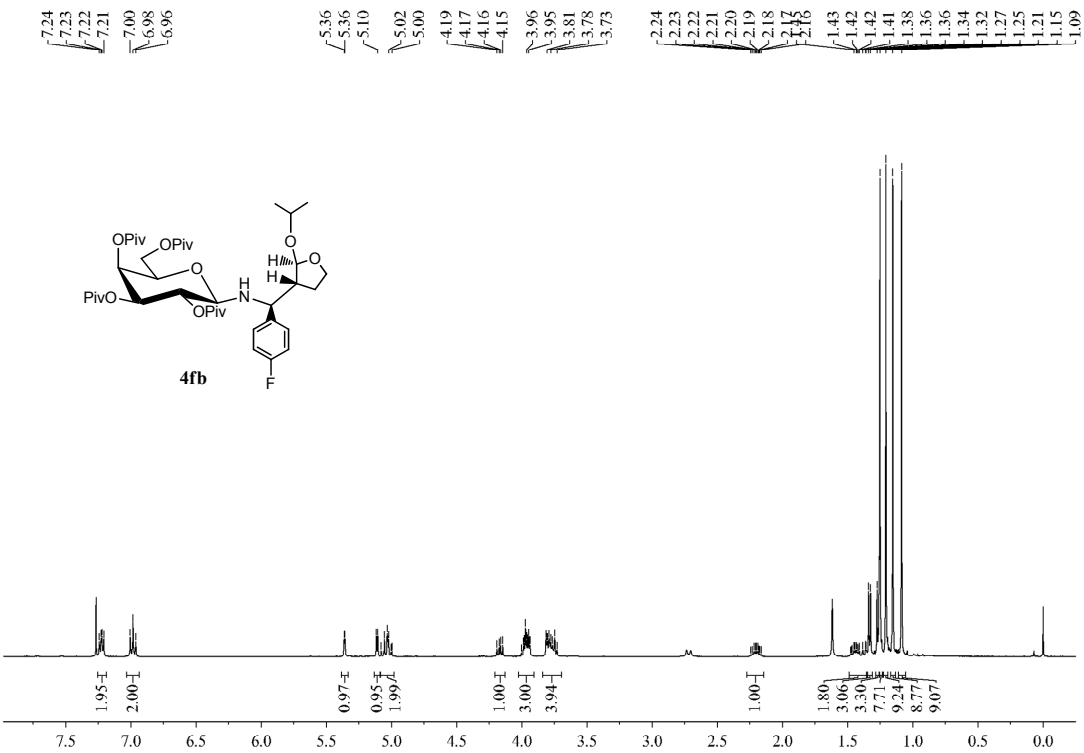
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1.25
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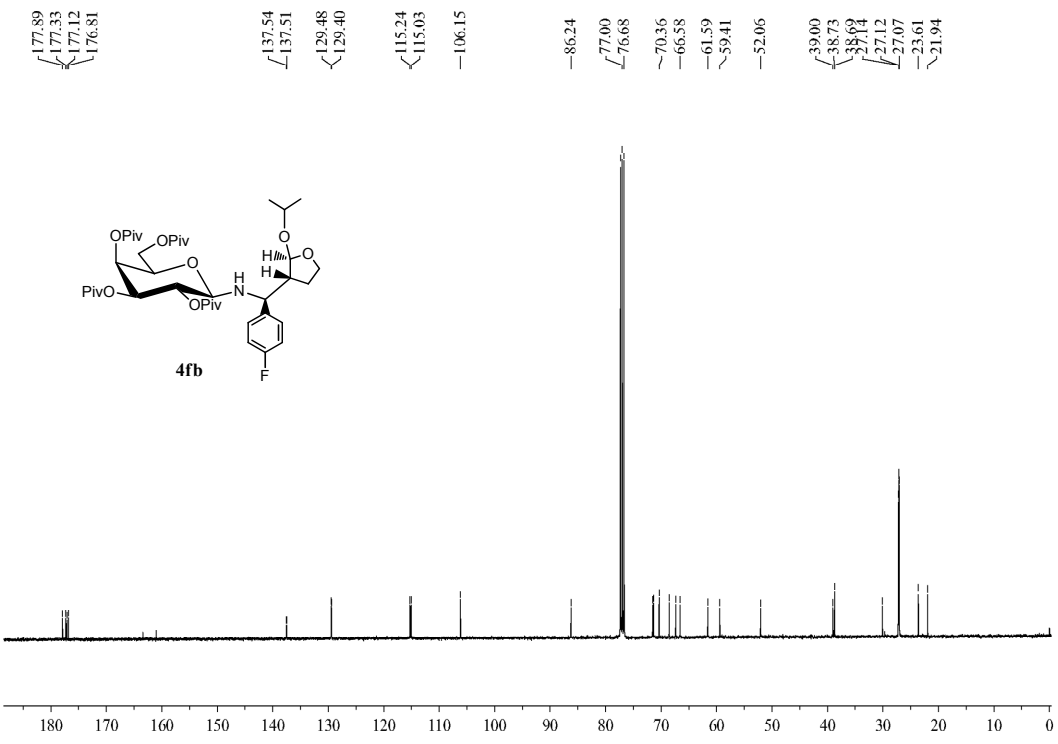
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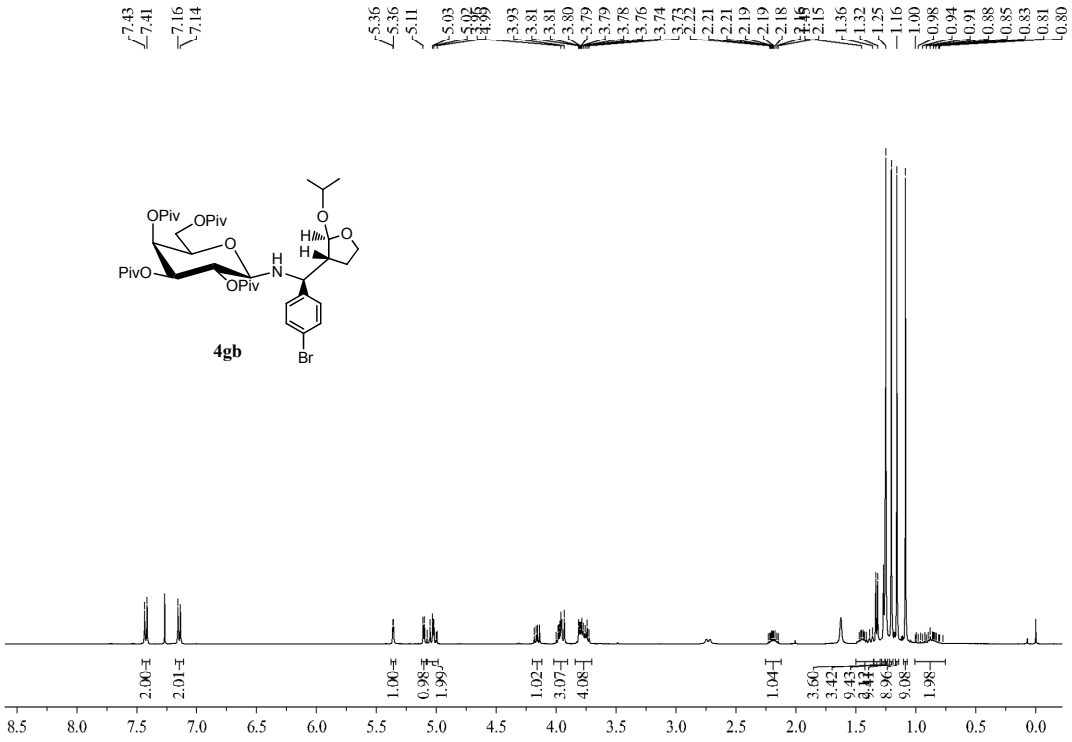
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Br
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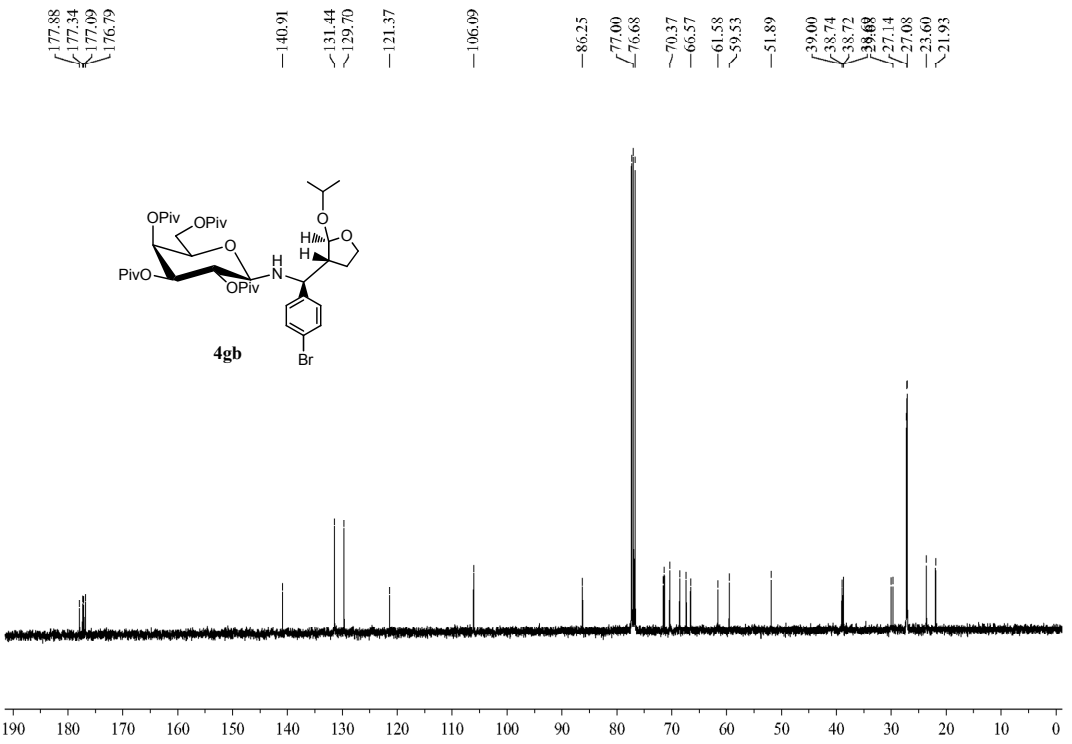
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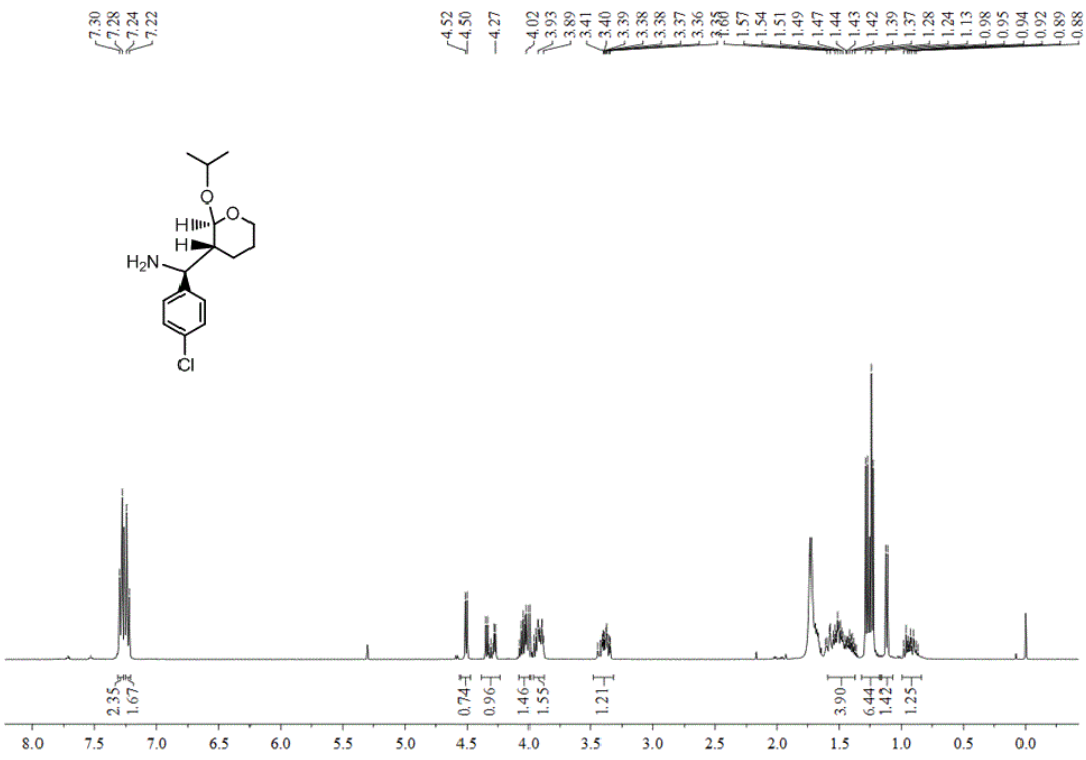
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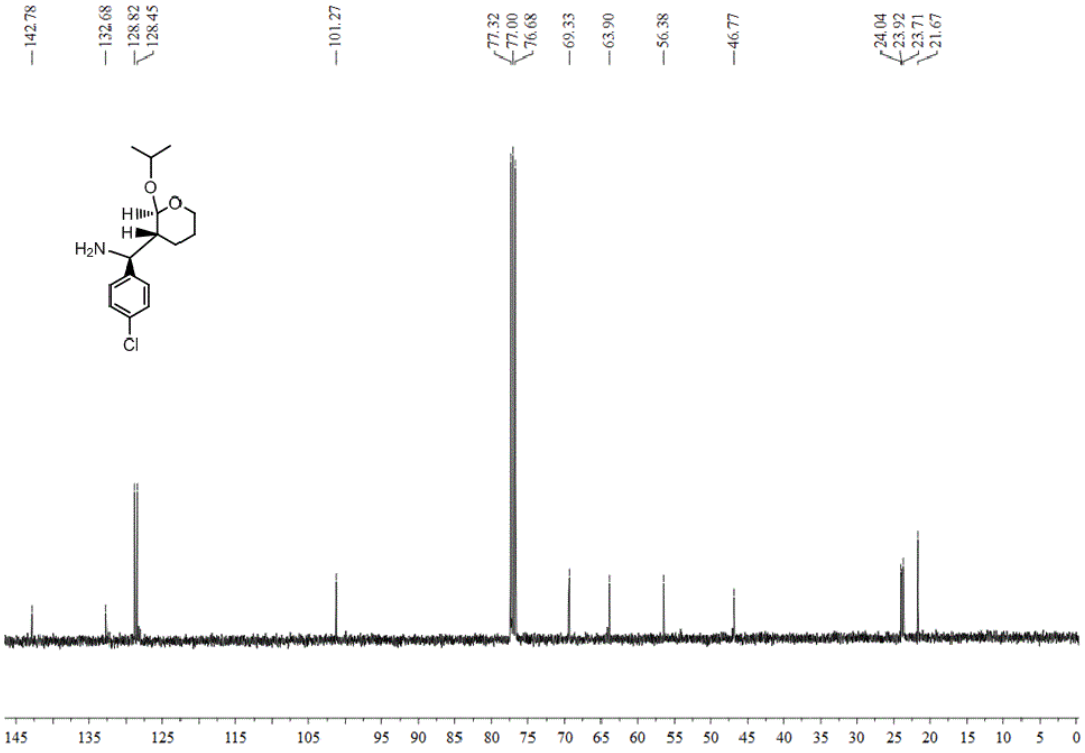
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H2N
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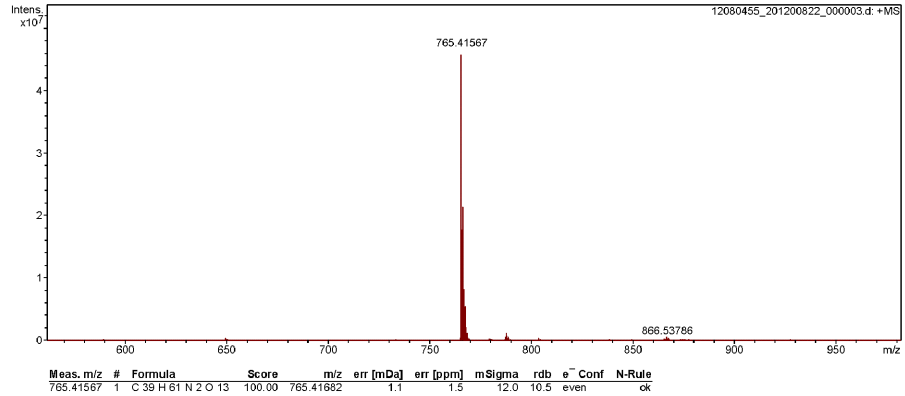
Copies of HR-ESI-MS spectra of 4 and 5

4aa

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080455_201200822_000003.d	Acquisition Date	8/22/2012 4:33:22 PM
Sample	WG-3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
765.41567	1	C 39 H 61 N 2 O 13	100.00	765.41682	1.1	1.5	12.0	10.5	even	ok

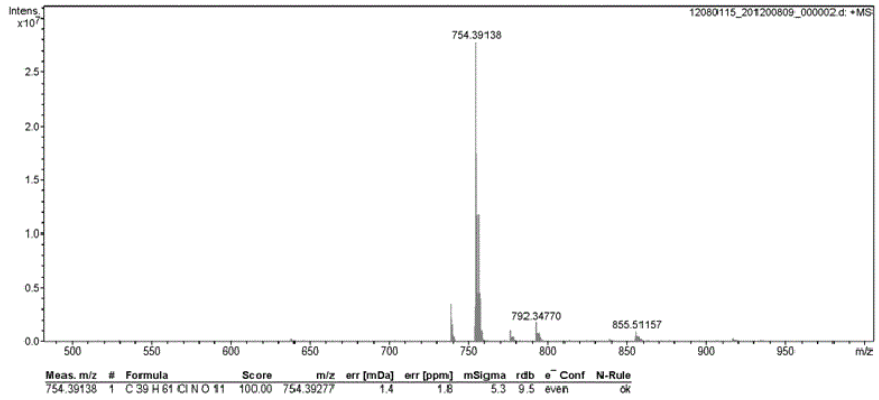
Bruker Compass DataAnalysis 4.0 printed: 8/22/2012 4:34:24 PM Page 1 of 1

4ba

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080115_201200809_000002.d	Acquisition Date	8/9/2012 2:59:46 PM
Sample	WG20120806-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
754.39138	1	C 39 H 61 Cl N O 11	100.00	754.39277	1.4	1.8	5.3	9.5	even	ok

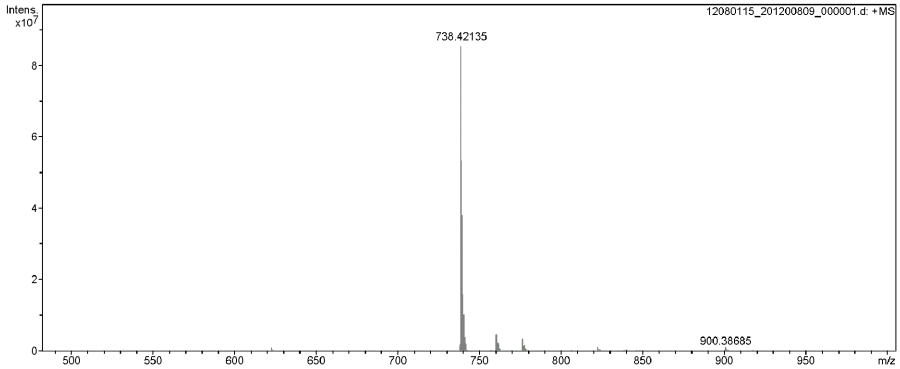
Bruker Compass DataAnalysis 4.0 printed: 8/9/2012 3:03:03 PM Page 1 of 1

4ca

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080115_201200809_000001.d	Acquisition Date	8/9/2012 2:58:46 PM
Sample	WG20120806-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



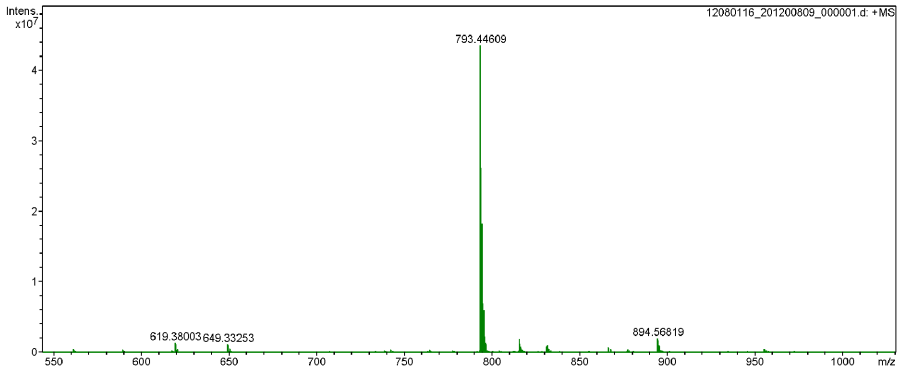
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
738.42135	1	C 39 H 61 F N O 11	100.00	738.42232	1.0	1.3	8.5	9.5	even	ok

4da

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080116_201200809_000001.d	Acquisition Date	8/9/2012 3:04:20 PM
Sample	YJ20120806-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



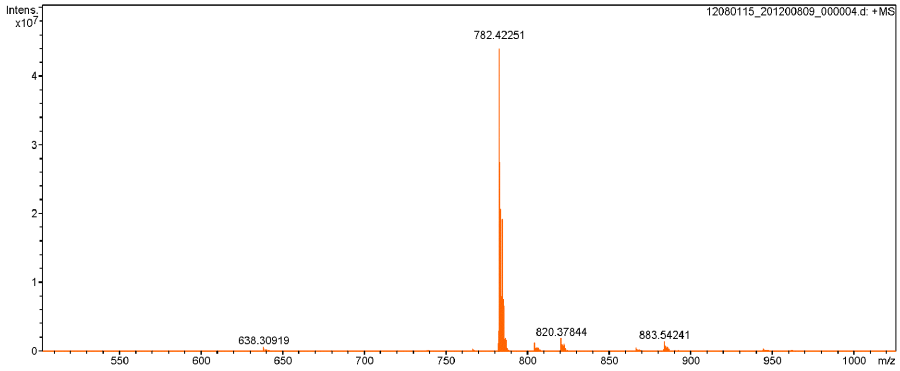
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
793.44609	1	C 41 H 65 N 2 O 13	100.00	793.44812	2.0	2.6	13.8	10.5	even	ok

4ea

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080115_201200809_000004.d	Acquisition Date	8/9/2012 3:01:53 PM
Sample	WG20120806-4	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



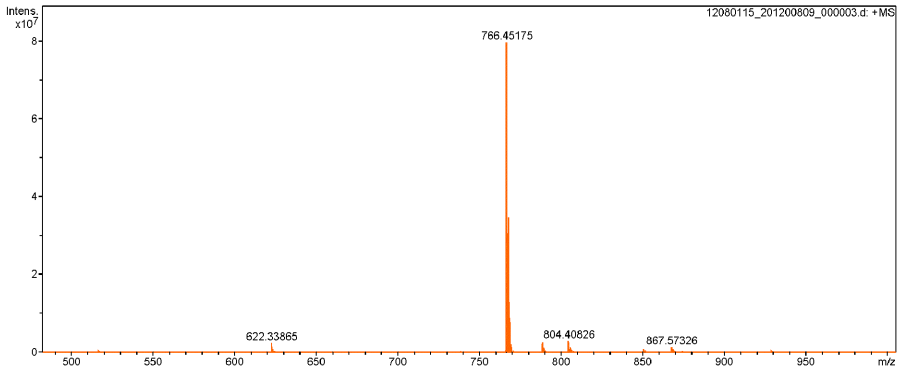
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
782.42251	1	C 41 H 65 Cl N O 11	100.00	782.42407	1.6	2.0	5.6	9.5	even	ok

4fa

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080115_201200809_000003.d	Acquisition Date	8/9/2012 3:00:46 PM
Sample	WG20120806-3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



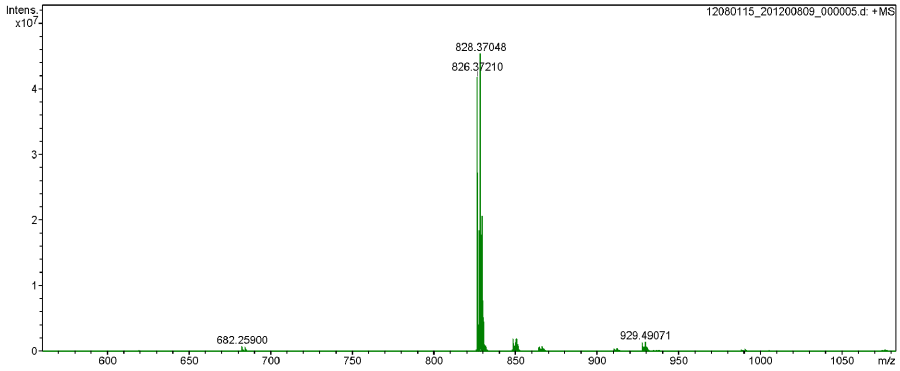
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
766.45175	1	C 41 H 65 F N O 11	100.00	766.45362	1.9	2.4	7.7	9.5	even	ok

4ga

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080115_201200809_000005.d	Acquisition Date	8/9/2012 3:02:49 PM
Sample	WG20120806-5	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



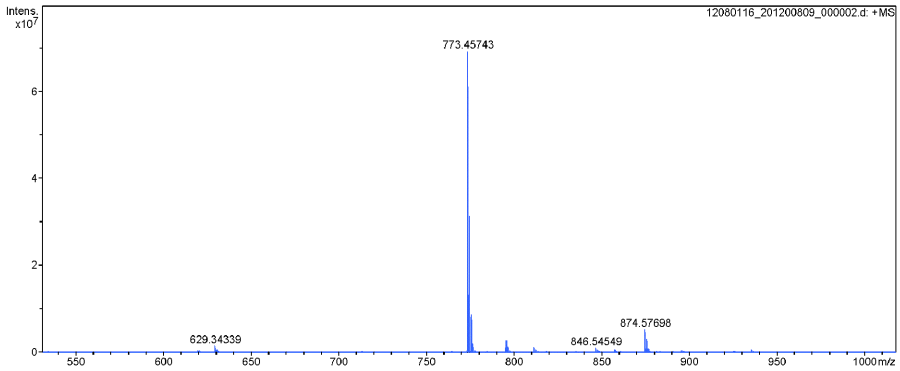
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
826.37210	1	C 41 H 65 Br N O 11	100.00	826.37355	1.4	1.8	12.1	9.5	even	ok

4ha

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080116_201200809_000002.d	Acquisition Date	8/9/2012 3:05:13 PM
Sample	YJ20120806-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



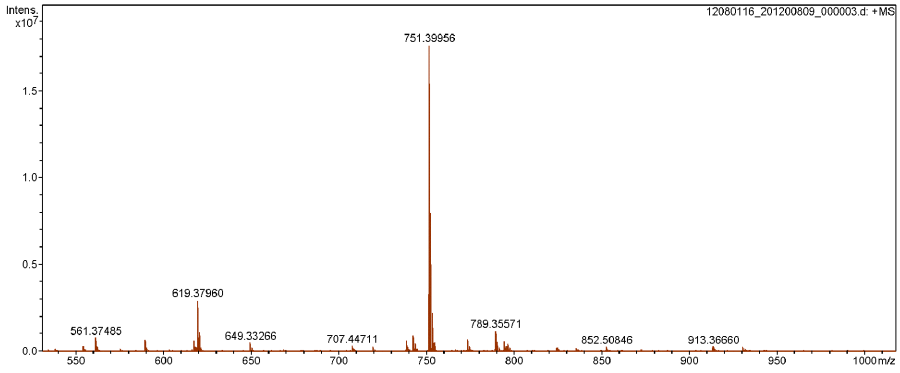
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
773.45743	1	C 42 H 65 N 2 O 11	100.00	773.45829	0.9	1.1	6.9	11.5	even	ok

4ab

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080116_201200809_000003.d	Acquisition Date	8/9/2012 3:07:08 PM
Sample	YJ20120806-3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



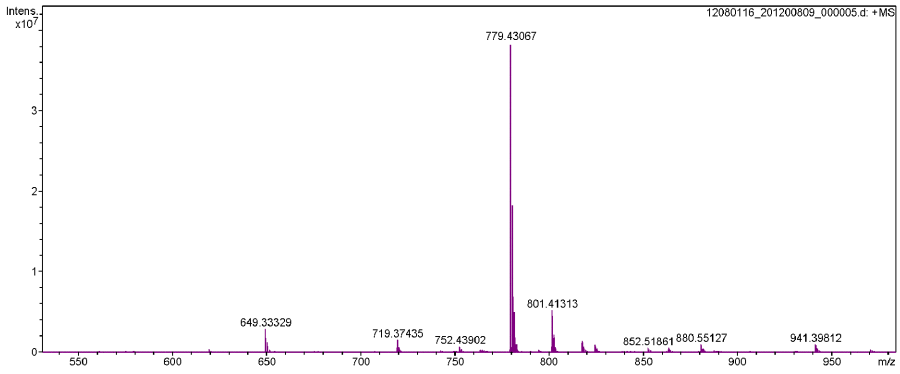
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
751.39956	1	C 38 H 59 N 2 O 13	100.00	751.40117	1.6	2.1	11.3	10.5	even	ok

4db

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080116_201200809_000005.d	Acquisition Date	8/9/2012 3:11:13 PM
Sample	YJ20120806-4	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



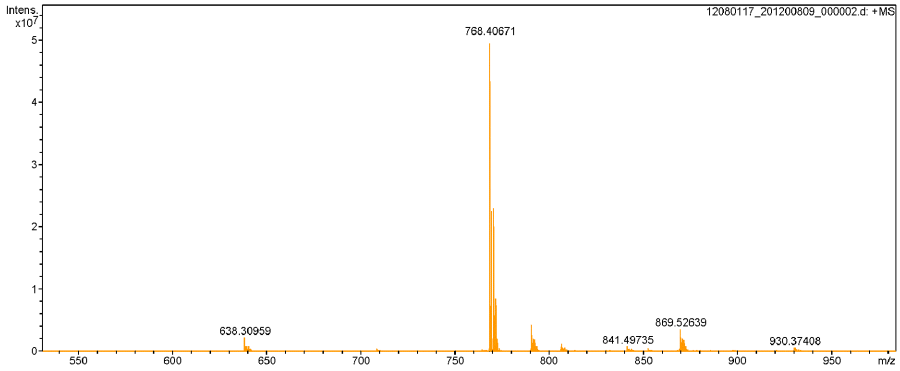
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
779.43067	1	C 40 H 63 N 2 O 13	100.00	779.43247	1.8	2.3	11.1	10.5	even	ok

4eb

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080117_201200809_000002.d	Acquisition Date	8/9/2012 3:12:23 PM
Sample	LW20120806-2	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



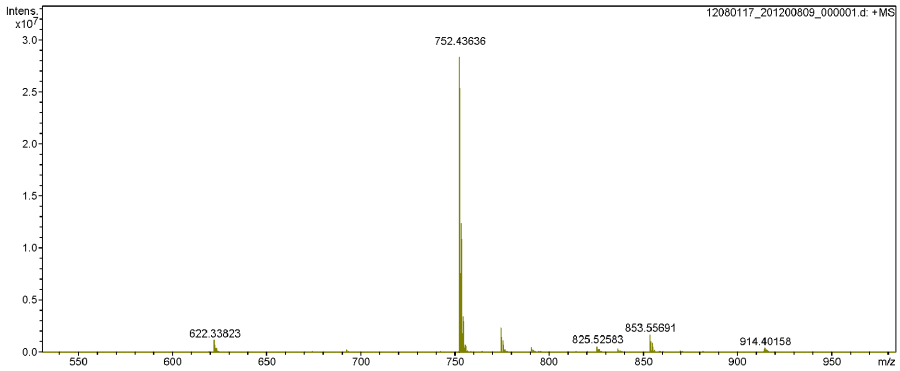
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
768.40671	1	C 40 H 63 Cl N O 11	100.00	768.40842	1.7	2.2	7.3	9.5	even	ok

4fb

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080117_201200809_000001.d	Acquisition Date	8/9/2012 3:09:40 PM
Sample	LW20120806-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



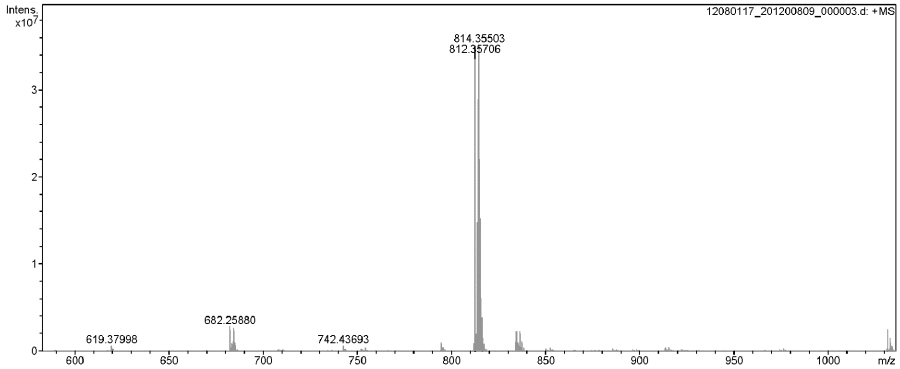
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
752.43636	1	C 40 H 63 F N O 11	100.00	752.43797	1.6	2.1	2.6	9.5	even	ok

4gb

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

Analysis Name	12080117_201200809_000003.d	Acquisition Date	8/9/2012 3:13:17 PM
Sample	LW20120806-3	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



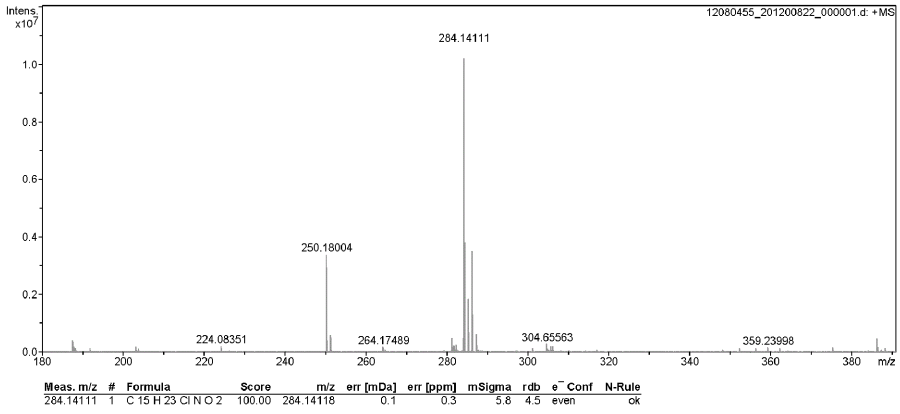
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
812.35706	1	C 40 H 63 Br N O 11	100.00	812.35790	0.8	1.0	27.8	9.5	even	ok

5ea

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info

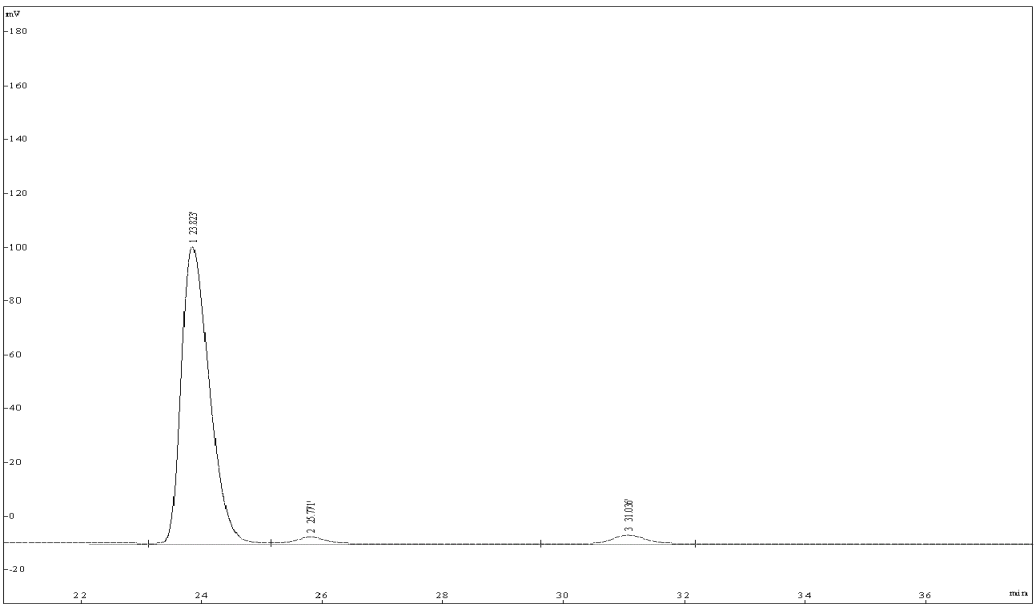
Analysis Name	12080455_201200822_000001.d	Acquisition Date	8/22/2012 4:31:00 PM
Sample	WG-1	Instrument	Bruker Apex IV FTMS
Comment	ESI Positive	Operator	Peking University



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
284.14111	1	C 15 H 23 Cl N O 2	100.00	284.14118	0.1	0.3	5.8	4.5	even	ok

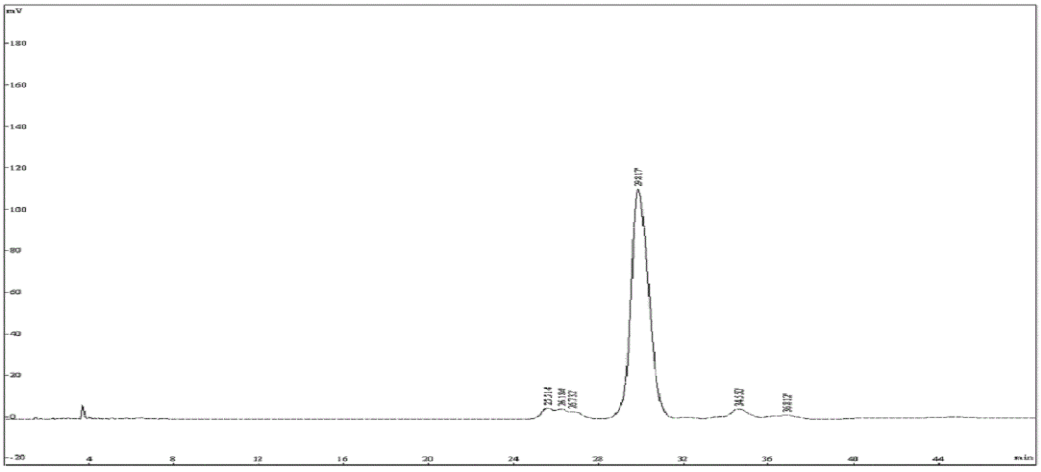
Copies of HPLC spectra of 4 and 5

4aa



Peak	Rettime	Area%	Area
1	23.823	90.17	3614834
2	25.771	5.019	201211
3	31.036	4.804	192593
Totals		100	4008638

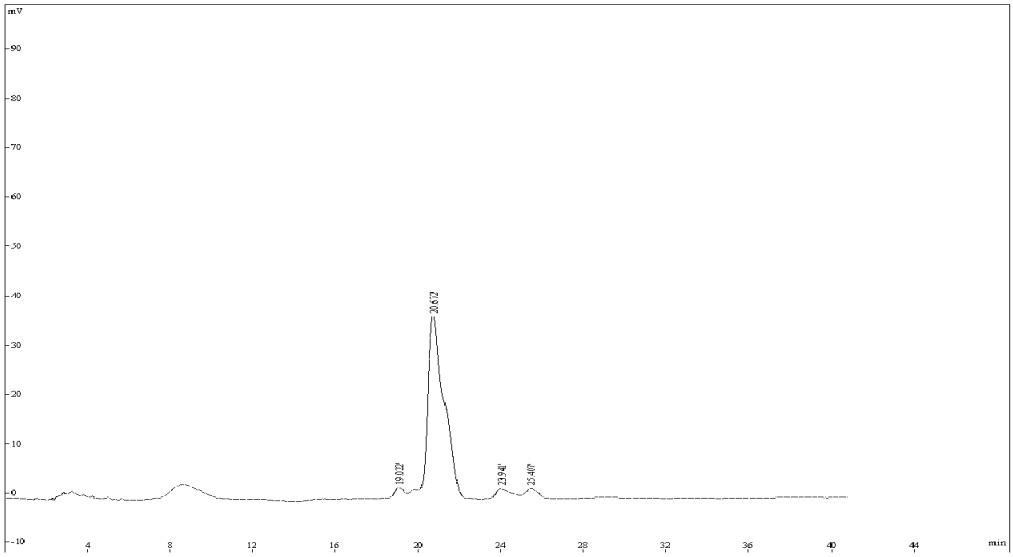
4ba



Sigal 1: DAD1 C, Sig=220,8 Ref=360,100

peak	RetTime	Area%	Area
1	25.514	3.351	265967
2	26.184	2.685	213073
3	26.732	2.116	167906
4	29.817	83.55	6630675
5	34.550	5.202	412853
6	36.812	3.103	246240
Totals		100	7936714

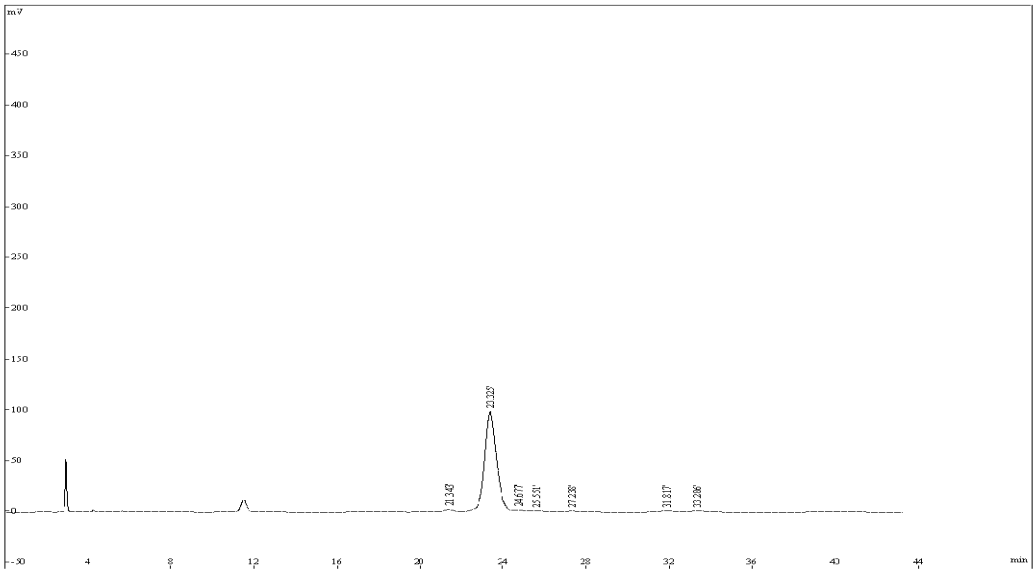
4ca



Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak	Rettime	Area%	Area
1	19.022	4.509	110458
2	20.672	86.12	2109634
3	23.941	5.058	123908
4	25.407	4.312	105630
Totals		100	2449630

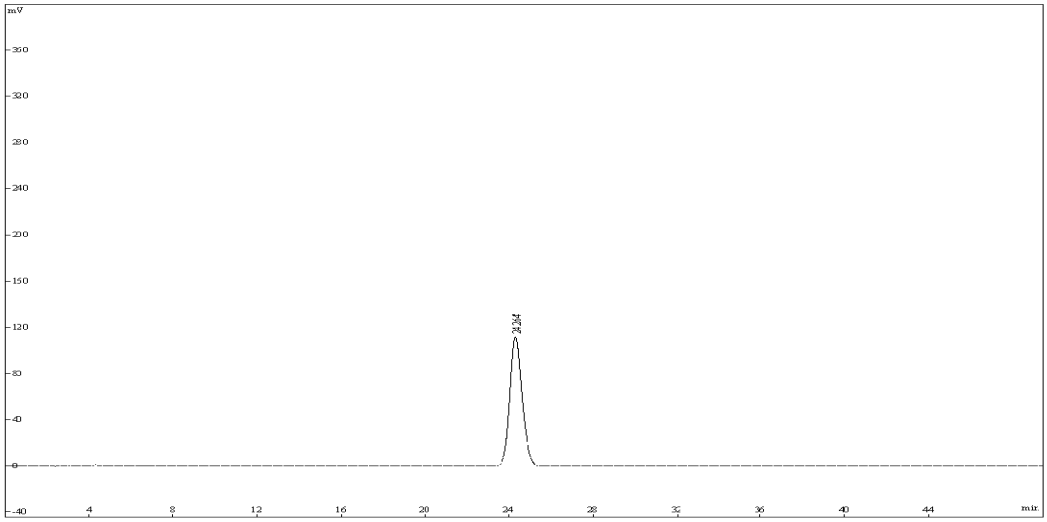
4da



Signal 1: DAD1 C, Sig=254,8 Ref=360,100

Peak	Rettime	Area%	Area
1	21.343	1.932	76972
2	23.325	92.42	3682034
3	24.677	1.61	64156
4	25.551	0.8164	32527
5	27.238	0.8566	34128
6	31.817	1.021	40680
7	33.286	1.345	53573
Totals		100	3984070

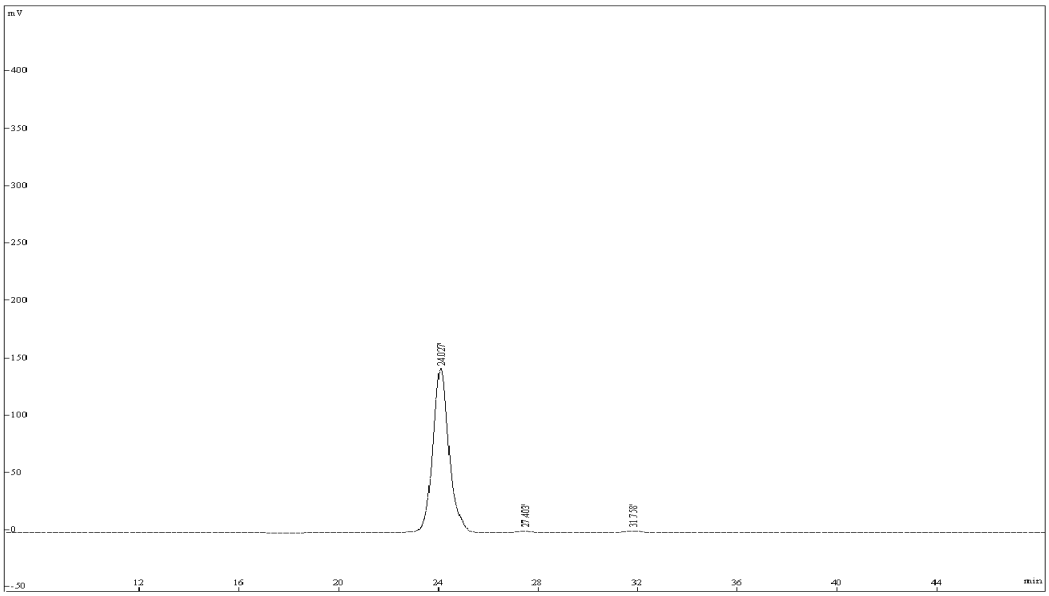
4da (after recrystallization)



Signal 1: DAD1 C, Sig=254,8 Ref=360,100

Peak	Rettime	Area%	Area
1	24.264	100	4641969
Totals		100	4641969

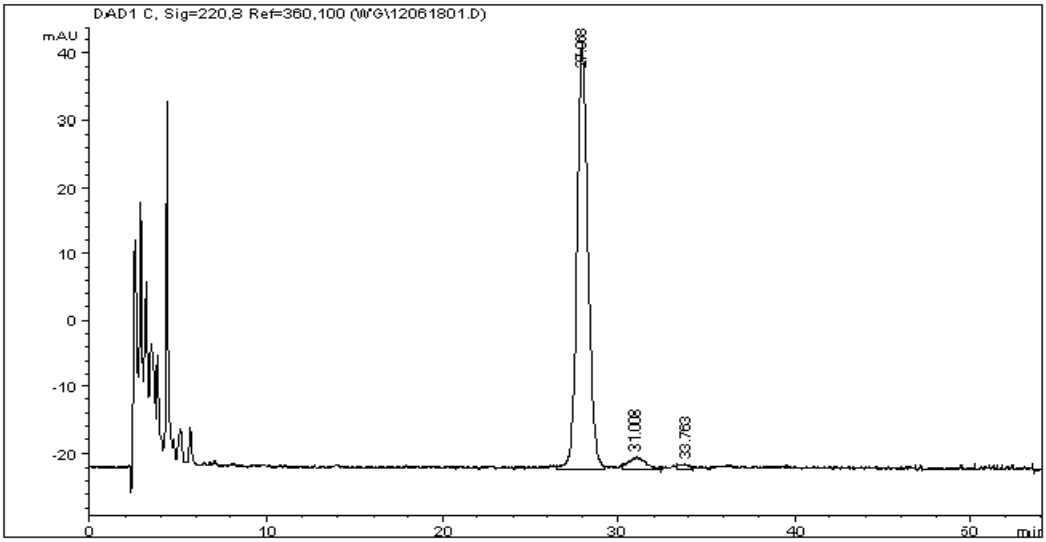
4ea



Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak	Rettime	Area%	Area
1	24.027	95.68	6736618
2	27.403	1.887	132856
3	31.758	2.432	171202
Totals		100	7040676

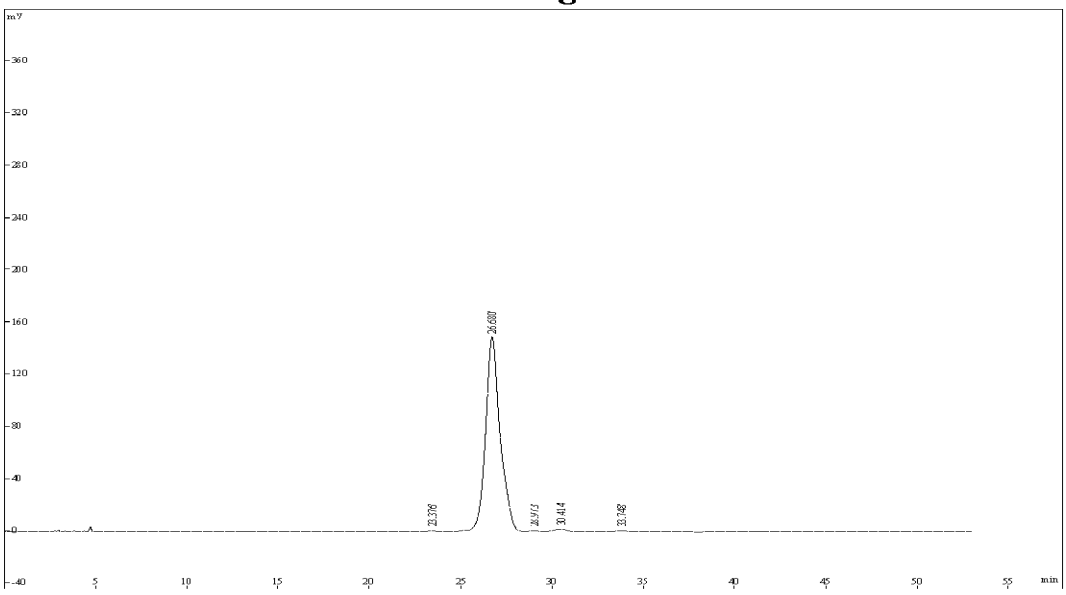
4fa



Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.968	VB	0.6445	2756.37280	62.99730	94.6991
2	31.008	VV	0.7762	119.92587	1.83093	4.1202
3	33.763	VV	0.4806	34.36559	8.52003e-1	1.1807
Totals :				2910.66427	65.68023	

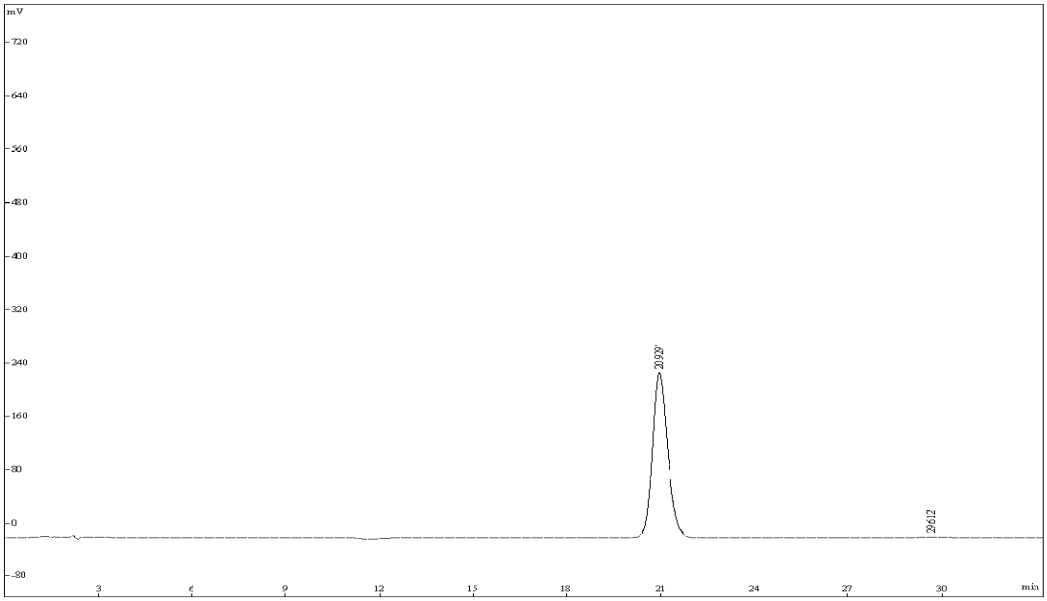
4ga



Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak	Rettime	Area%	Area
1	23.376	1.036	91153
2	26.680	94.65	8326867
3	28.973	0.912	80238
4	30.414	2.001	176055
5	33.748	1.401	123259
Totals		100	8797572

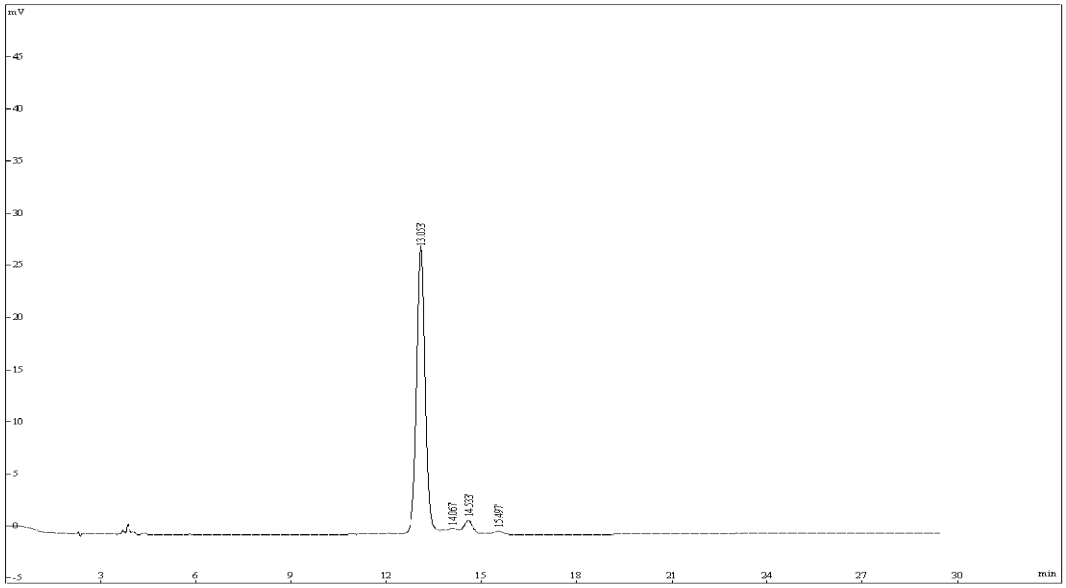
4ha



Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak	Rettime	Area%	Area
1	20.929	96.7	8800029
2	29.612	3.3	300270
Totals		100	9100299

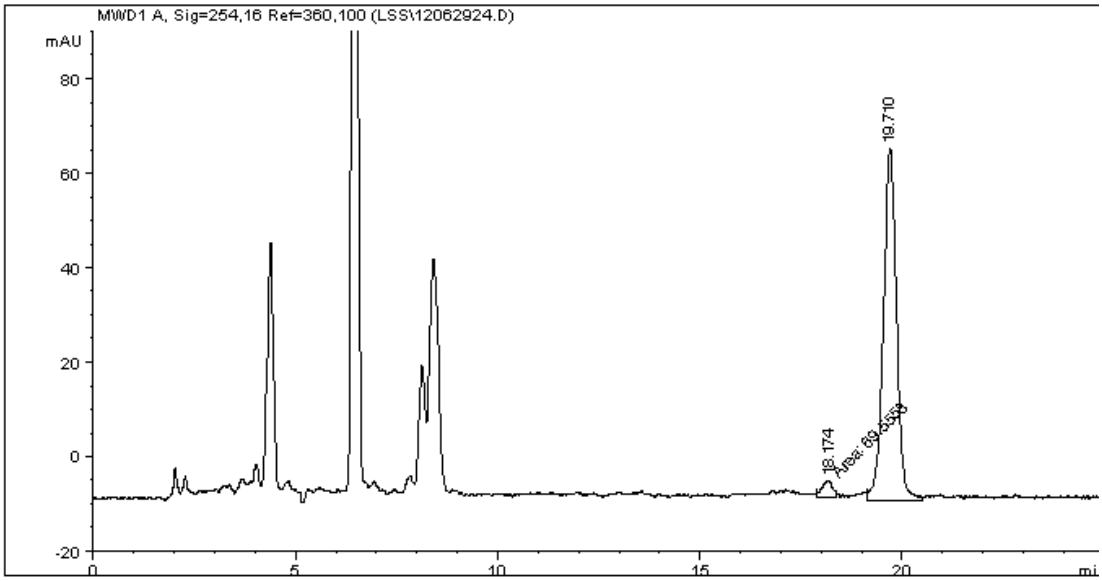
4ab



Signal 1: DAD1 C, Sig=254,8 Ref=360,100

Peak	Rettime	Area%	Area
1	13.053	90.65	520372
2	14.067	2.19	12573
3	14.533	5.675	32578
4	15.497	1.477	8477
Totals		100	574000

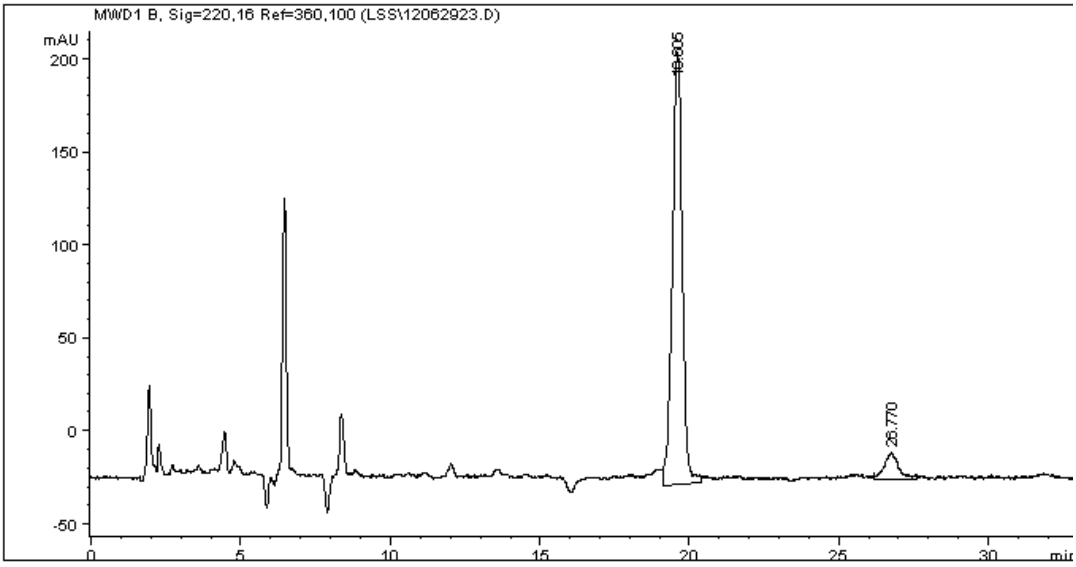
4db



Signal 1: MWD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.174	MM	0.3103	69.55581	3.73634	3.9071
2	19.710	VV	0.3534	1710.66443	74.62594	96.0929
Totals :				1780.22024	78.36228	

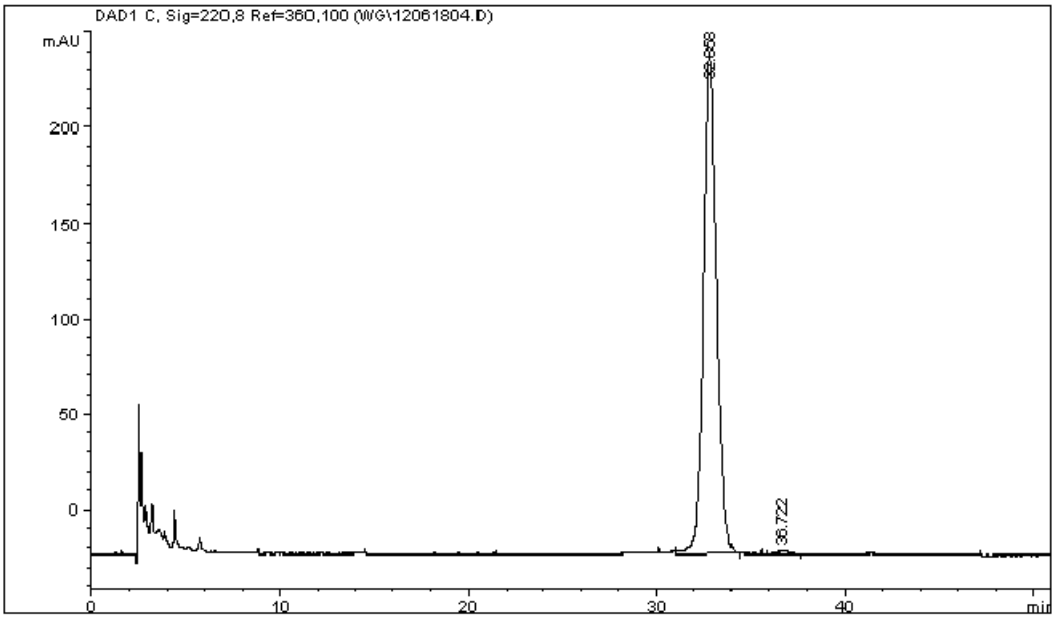
4fb



Signal 1: MWD1 B, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.605	VB	0.3613	5346.06006	231.59770	91.9950
2	26.770	BB	0.4050	465.18750	13.95255	8.0050
Totals :				5811.24756	245.55025	

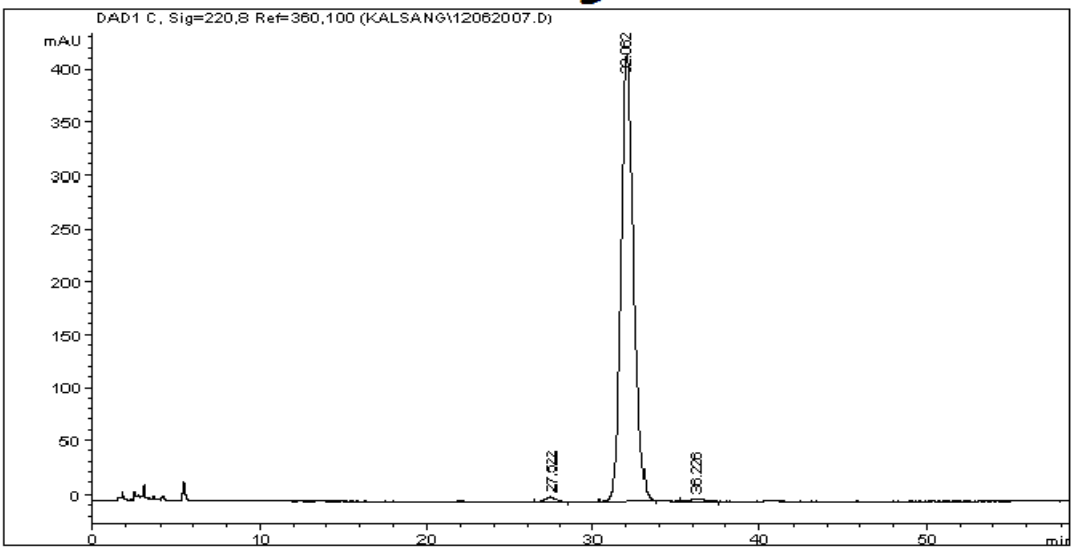
4eb



Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.858	VB	0.7278	1.28518e4	260.38528	99.0646
2	36.722	VP	0.6237	121.34687	2.31445	0.9354
Totals :				1.29731e4	262.69973	

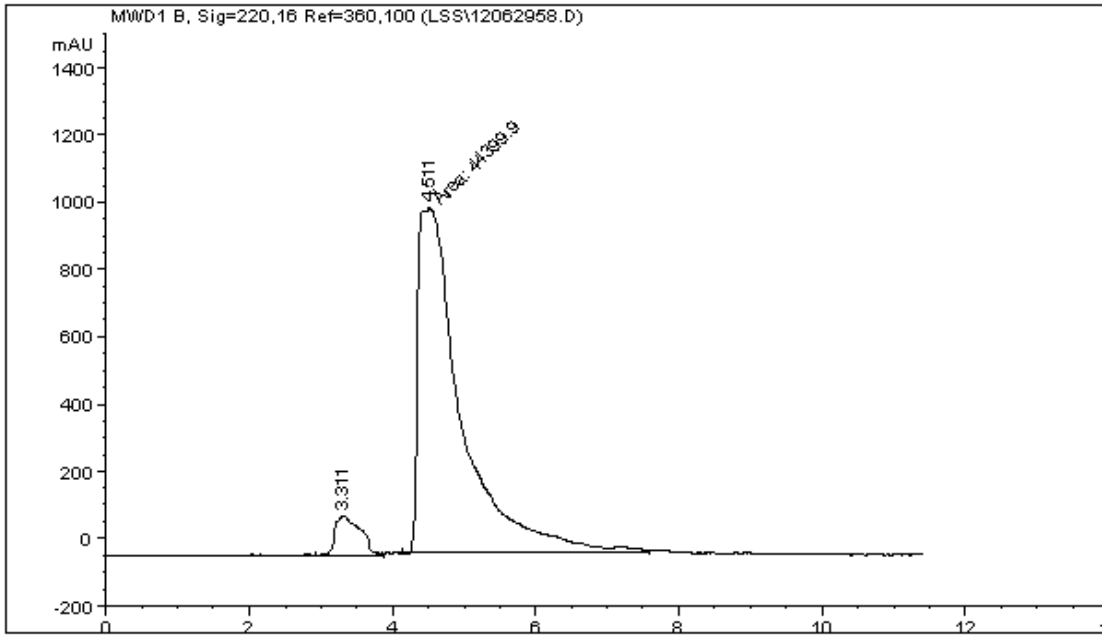
4gb



Signal 1: DAD1 C, Sig=220,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.522	BV	0.5330	176.36844	3.96467	0.7741
2	32.062	VB	0.8070	2.24747e4	419.55173	98.6380
3	36.226	BP	0.6718	133.96820	2.37587	0.5880
Totals :				2.27851e4	425.89227	

5ea



Signal 1: MWD1 B, Sig=220,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.311	VV	0.3194	2854.19727	115.87192	6.0401
2	4.511	MM	0.7209	4.43999e4	1026.49707	93.9599
Totals :				4.7254le4	1142.36899	